



DECLARATION

I, Maemi NAKANISHI, declare that I reside at 38-1-A106, Machikaneyama-cho, Toyonaka-shi, OSAKA 560-0043 JAPAN; That I am familiar with the English and Japanese languages;

That I have prepared a translation of Japanese Patent Application No. 143536/1998, "酸感応性化合物及びフォトレジスト用樹脂組成物, ACID-RESPONSIVE COMPOUNDS AND RESIN COMPOSITIONS FOR PHOTORESIST"; said translation thereof being attached hereto and made a part of this declaration;

That to the best of my knowledge and belief, the attached translation is accurate and fairly reflects the contents and meaning of the foregoing Japanese language document.

I declare, under penalty of perjury under the laws of the United States of America, that the foregoing is true and correct.

Executed, on August 30, 2001.

Maemi Nakanishi  
Maemi NAKANISHI

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This is to certify that the annexed is a true copy  
of the following application as filed with this Office.

Date of Application: May 25, 1998

Application Number: 143536/1998

Applicant(s): Daicel Chemical Industries, Ltd.

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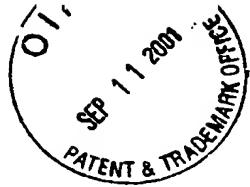
June 11, 1999

Commissioner,

Patent Office

Takeshi ISAYAMA

Certification No. 3037505/1999



- 1 -

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COMPOUNDS AND RESIN  
COMPOSITIONS FOR  
PHOTORESIST  
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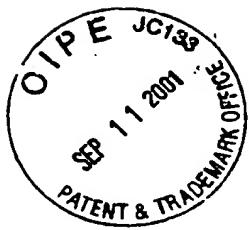
[Attached Documents]

[Item] Specification one copy

[Item] Abstract one copy

[Identification No. of General Power] 9001562

[Requirement of Proof] Yes



- 1 -

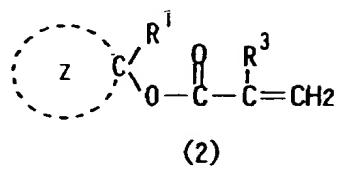
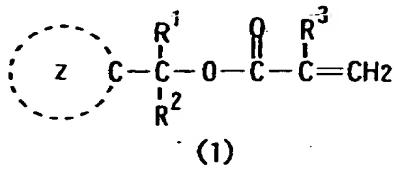
[Document Name] SPECIFICATION

[Title of the Invention] ACID-RESPONSIVE COMPOUNDS AND RESIN COMPOSITIONS FOR PHOTORESIST

[Claims]

[Claim 1] An acid-responsive compound represented by the following formula (1) or (2):

[Formula 1]



wherein R<sup>1</sup> represents a branched-chain alkyl group having a tertiary carbon atom, or a cycloalkyl group; R<sup>2</sup> represents hydrogen atom or an alkyl group; R<sup>3</sup> represents hydrogen atom or methyl group; and the ring Z represents a monocyclic or polycyclic alicyclic hydrocarbon ring which may have a substituent.

[Claim 2] An acid-responsive compound according to Claim 1, wherein R<sup>1</sup> has a tertiary carbon atom in the 1-position.

[Claim 3] An acid-responsive compound according to Claim 1, wherein R<sup>1</sup> is a 1-C<sub>1-2</sub>alkyl-C<sub>1-4</sub>alkyl group.

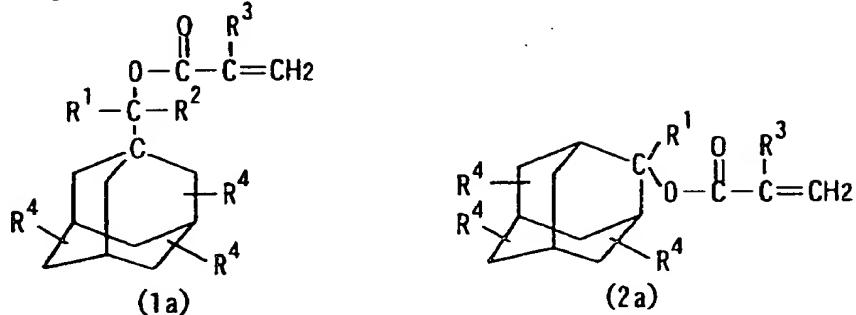
[Claim 4] An acid-responsive compound according to Claim 1, wherein the ring Z is a bridged-ring hydrocarbon ring containing 2 to 4 component rings.

[Claim 5] An acid-responsive compound according to

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Claim 1 represented by the following formula (1a) or (2a):

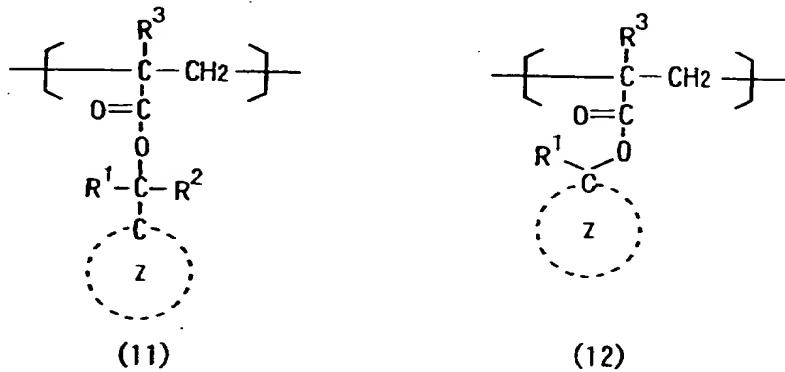
[Formula 2]



wherein the groups R<sup>4</sup>'s are the same or different from each other, each representing hydrogen atom, a halogen atom, an alkyl group, oxo group, hydroxyl group, an alkoxy group, carboxyl group, an alkoxy carbonyl group, hydroxymethyl group, carbamoyl group, an N-substituted carbamoyl group, nitro group, amino group, an N-substituted amino group; these groups may be protected with a protective group; and R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> have the same meanings as defined above.

[Claim 6] A photoresist resin composition comprising a polymer containing at least a unit represented by the formula (11) or (12):

[Formula 3]



wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and the ring Z have the same meanings as defined above

and a photoactive acid generator.

[Claim 7] A photoresist resin composition according to Claim 6, wherein the polymer is a copolymer.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to acid-responsive compounds including adamantane derivatives and to photoresist resin compositions prepared using the acid-responsive compounds. More particularly, the present invention relates to a photoresist resin composition suitable for the formation of a pattern (e.g. minute (fine) processing of semiconductor) using ultraviolet rays or far-ultraviolet rays (inclusive of excimer laser beams) and an acid-responsive compound therefor.

[0002]

[Background Art]

The semiconductor integrated circuit is fabricated by a lithographic process which comprises forming a resist thin-layer on a substrate, then forming a latent image pattern by imagewise exposure to light, developing the latent image to form a resist pattern, dry-etching the substrate using the resist pattern as a mask, and removing the resist to provide a designed pattern.

[0003]

As the resist for semiconductor manufacture, a

photosensitive resin composition containing an alkali-soluble novolac resin and a diazonaphthoquinone derivative is known. This resin composition has been used as a positive-acting resist by taking advantage of the phenomenon that on exposure to light the diazonaphthoquinone group is decomposed to give a carboxyl group, whereby the composition which is initially alkali-insoluble is rendered alkali-soluble. There also is known a negative-acting resist, that is a resist which becomes insoluble on exposure to light through a photo-crosslinking reaction in the presence of an azide compound or a photopolymerization reaction in the presence of a photopolymerization initiator.

Meanwhile, in the lithographic technology, the demand for a finer line pattern definition has caused a shift from ultraviolet rays, such as g-line and i-line, to rays of shorter wavelengths, such as far-ultraviolet rays, vacuum ultraviolet rays, excimer laser beams, an electron beam and X-rays.

However, because the resins used contain an aromatic ring, those resists may at times be opaque to light at wavelengths shorter than 200 nm and are not suited (inactive) as compositions for use with an ArF excimer laser which has a wavelength of 193 nm.

[0004]

As a photoresist suitable for short-wavelength exposure light sources (e.g. ArF excimer laser), Japanese

Patent Application Laid-Open No, 73173/1997 discloses a resist material comprising a polymer having a structural unit protected by an alicyclic hydrocarbon group, such as adamantane or norbornane, which is cleaved (eliminated) by an acid to render the material alkali-soluble in combination with an acid precursor. This literature mentions, as the polymer, (1) a copolymer of 2-methyl-2-adamantyl (meth)acrylate and (2) a copolymer of 2-(1-adamantyl)propyl (meth)acrylate, among others. The above polymer having no double bond within its ring structure is transparent (active) to the ArF excimer laser beam and, in semiconductor fine processing, the resistance to plasma gas dry-etching is enhanced.

[0005]

However, when the above resist comprising the polymer and the acid precursor is used to form a pattern, the tendency toward formation of cracks and peeling of the pattern is increased as the pattern line becomes finer so that it is sometimes impossible to form a pattern of fine line definition.

[0006]

[Problems to be Solved by the Invention]

The present invention, therefore, has for its object to provide an acid-responsive compound having an alicyclic hydrocarbon group (e.g. an adamantane skeleton) and capable of providing an alkali-soluble polymer on exposure to light, thus being useful for the formation of fine-

line patterns and a photoresist resin composition containing the compound.

It is another object of the present invention to provide an acid-responsive compound which is high in sensitivity and etching resistance (particularly resistance to dry etching) and instrumental in forming a fine-line resist pattern with good reproducibility and high precision and a photoresist resin composition containing the compound.

It is still another object of the present invention to provide an acid-responsive compound showing high adhesion to a substrate and useful for forming a fine-line resist pattern with high precision and high reproducibility and a photoresist resin composition containing the compound.

[0007]

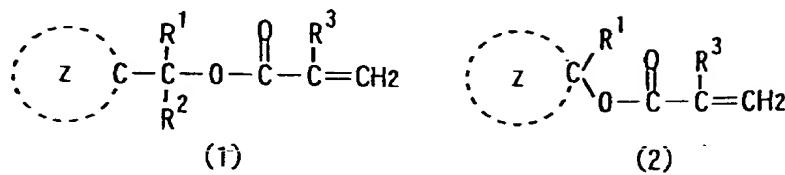
[Means to Solve the Problems]

The inventors of the present invention did intensive investigations for accomplishing the above objects and found that when a polymer comprising an acid-responsive compound unit having an alicyclic hydrocarbon group and a specific structure is used in combination with a photoactive acid precursor, the alicyclic hydrocarbon group is stably and efficiently eliminated from the polymer by the acid formed from the acid precursor on exposure to light to thereby enable water or alkali development. The present invention has been developed on the basis of the above finding.

The acid-responsive compound according to the present invention, therefore, is represented by the following formula (1) or (2):

[0008]

[Formula 4]

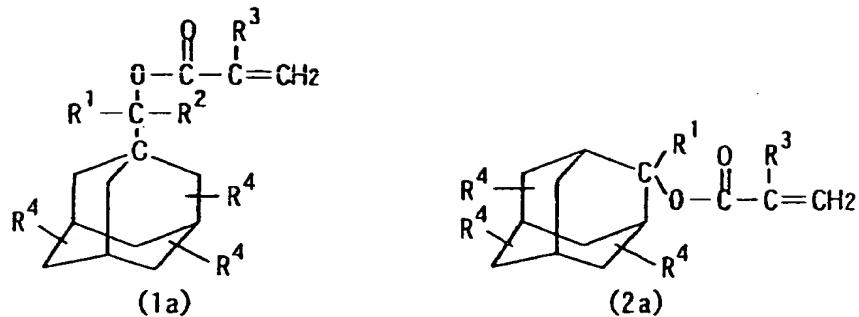


wherein R<sup>1</sup> represents a branched-chain alkyl group having a tertiary carbon atom, or a cycloalkyl group; R<sup>2</sup> represents hydrogen atom or an alkyl group; R<sup>3</sup> represents hydrogen atom or methyl group; and the ring Z represents a monocyclic or polycyclic alicyclic hydrocarbon ring which may have a substituent.

In this acid-responsive compound, R<sup>1</sup> may be an alkyl group having a methine carbon atom (tertiary carbon atom) in the  $\alpha$ -position (1-position) (e.g., 1-C<sub>1-2</sub>alkyl-C<sub>1-4</sub>alkyl groups), the ring Z may be a bridged-ring hydrocarbon ring (e.g., adamantane rings). Such compound includes adamantane derivatives represented by the following formula (1a) or (2a).

[0009]

[Formula 5]

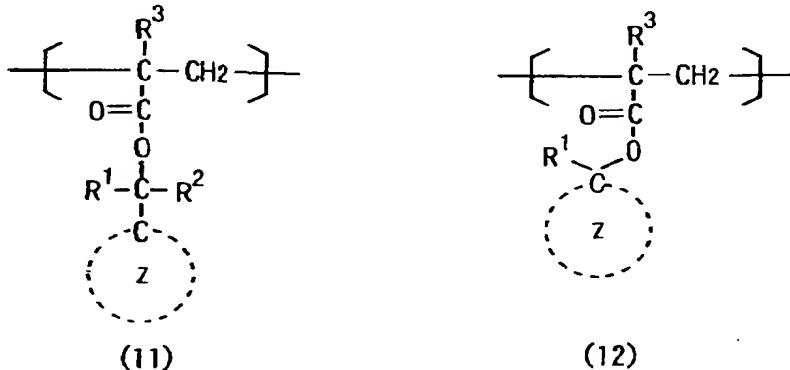


wherein the groups  $R^4$  are the same or different, each representing a substituent which may be protected by a protective group. The groups  $R^1$ ,  $R^2$ , and  $R^3$  have the same meanings as defined above.

The photoresist resin composition of this invention can be constituted of a polymer containing at least a unit represented by the formula (11) or (12):

[0010]

[Formula 6]



wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and the ring  $Z$  have the same meanings as defined above

and a photoactive acid generator.

[0011]

[Preferred Embodiment of the Invention]

In the formulae (1), (2), (1a), (2a), (11) and (12), examples of the branched-chain alkyl group having a tertiary carbon atom designated by  $R^1$  are  $1-C_{1-4}alkyl-C_{1-6}alkyl$  groups, such as isopropyl, isobutyl, 1-methylethyl, isopentyl, 1-methylpropyl (s-butyl), 1-methylbutyl (s-pentyl), s-hexyl, 1-ethylethyl, and 1-ethylbutyl. Included among the preferred branched-chain alkyl groups are alkyl groups in which  $R^1$  has a methine carbon atom in the  $\alpha$ -position, particularly  $1-C_2alkyl-C_{1-4}alkyl$  groups (e.g., isopropyl, s-butyl group).

[0012]

As the cycloalkyl group, there can be exemplified  $C_{3-10}cycloalkyl$  groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexyl, cyclooctyl, and cyclodecyl groups.

[0013]

The alkyl group designated by  $R^2$  includes  $C_{1-4}alkyl$  groups such as methyl and ethyl groups (particularly, methyl, ethyl groups).  $R^2$  is usually a hydrogen atom or a methyl group.  $R^3$  is a hydrogen atom or a methyl group, forming an acryloyl or methacryloyl group.

[0014]

The Z ring includes a variety of alicyclic hydrocarbon rings, for example, monocyclic hydrocarbon rings and polycyclic hydrocarbon rings (spiro hydrocarbon ring, ring assembly hydrocarbon ring, fused-ring hydrocarbon ring, and bridged-ring hydrocarbon ring. The

monocyclic hydrocarbon ring includes but is not limited to C<sub>4-10</sub> cycloalkane rings such as cycloheptane, cyclohexane, cyclopentane, cyclooctane, etc. and the spiro hydrocarbon ring includes but is not limited to C<sub>8-16</sub> hydrocarbon rings such as spiro[4.4]nonane, spiro[4.5]decane, spirobicyclohexane, etc. The ring assembly hydrocarbon ring includes but is not limited to hydrocarbon rings having C<sub>5-12</sub> cycloalkane rings, such as bicyclohexane ring, biperhydronaphthalene ring, etc. The fused-ring hydrocarbon ring includes, for example, fused-ring rings containing 5 to 8-membered cycloalkane component rings such as perhydronaphthalene ring (decalin ring), perhydroanthracene ring, perhydrophenanthrene ring, perhydroacenaphthene ring, perhydrofluorene ring, perhydroindene ring, perhydrophenalene ring, etc.

[0015]

The preferred Z ring is a bridged-ring hydrocarbon ring. The bridged-ring hydrocarbon ring includes but is not limited to bicyclic hydrocarbon rings such as pinane, bornane, norpinane, norbornane, etc.; tricyclic hydrocarbon rings such as homobrendane, adamantane, tricyclo[5.2.1.0<sup>2,6</sup>]decane, tricyclo[4.3.1.1<sup>2,5</sup>]undecane, etc.; tetracyclic hydrocarbon rings such as tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodecane, perhydro-1,4-methano-5,8-methanonaphthalene, etc.; hydrogenated dimers of dienes [e.g. hydrogenated dimers of cycloalkadienes such as cyclopentadiene, cyclohexadiene,

cycloheptadiene, etc. (e.g. perhydro-4,7-methanoindene etc.), butadiene dimer (vinylcyclohexene) and its hydrogenation product, and butadiene-cyclopentadiene dimer (vinylnorbornene) and its hydrogenation product]. The preferred bridged-ring hydrocarbon ring usually has a bornane, norbornane or adamantane skeleton.

The preferred Z ring is a bridged-ring hydrocarbon ring containing 2 to 4 component rings.

[0016]

These rings Z (monocyclic or polycyclic hydrocarbon rings) may have a substituent. As the substituent  $R^4$  of the ring Z, examples of which are hydrogen atom; halogen atoms (e.g., bromine, chlorine, fluorine), alkyl groups ( $C_{1-4}$ alkyl groups such as methyl, ethyl, butyl, and t-butyl); oxo group; hydroxyl group; alkoxy groups ( $C_{1-4}$ alkoxy groups such as methoxy, ethoxy, t-butoxy); carboxyl group, alkoxy carbonyl groups ( $C_{1-4}$ alkoxycarbonyl groups such as methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, t-butoxycarbonyl groups); hydroxymethyl group; carbamoyl group; N-substituted carbamoyl groups (e.g.,  $N-C_{1-4}$ alkylcarbamoyl groups); nitro group; amino group; and N-substituted amino groups (e.g., mono- or di $C_{1-4}$ alkylamino groups).

[0017]

These substituent groups  $R^4$  each may be protected with a protective group, and this protective group may be a protective group which can be eliminated with an acid,

that is to say, a protective group which functions as a dissolution-inhibitory modifying group for preventing dissolution of the polymer prior to exposure to light.

The protective group for hydroxyl group and hydroxymethyl group includes but is not limited to alkoxy carbonyl groups ( $C_{1-4}$  alkoxy carbonyl groups such as methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl, etc.) and benzyloxy group.

The protective group for carboxyl group includes but is not limited to alkoxy groups ( $C_{1-4}$  alkoxy groups such as methoxy, ethoxy, t-butoxy, etc.), aralkyloxy groups (benzyloxy, p-methoxybenzyloxy, diphenylmethyloxy, benzhydryloxy, etc.) and N-hydroxysuccinimido group.

[0018]

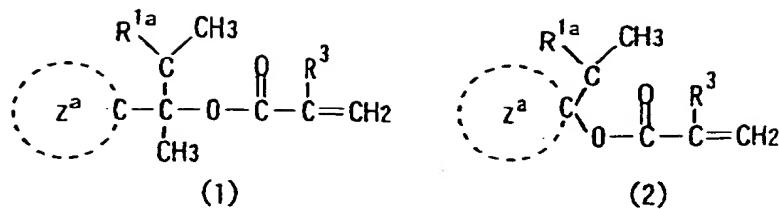
When each of these substituent  $R^4$  represents hydroxyl group, carboxyl group, hydroxymethyl group, carbamoyl group, or amino group (particularly, hydroxyl group or carboxyl group), the adhesion between the resist and the substrate is improved.

[0019]

Included among the preferred acid-responsive compounds are (meth)acrylates represented by the following formulae:

[0020]

[Formula 7]

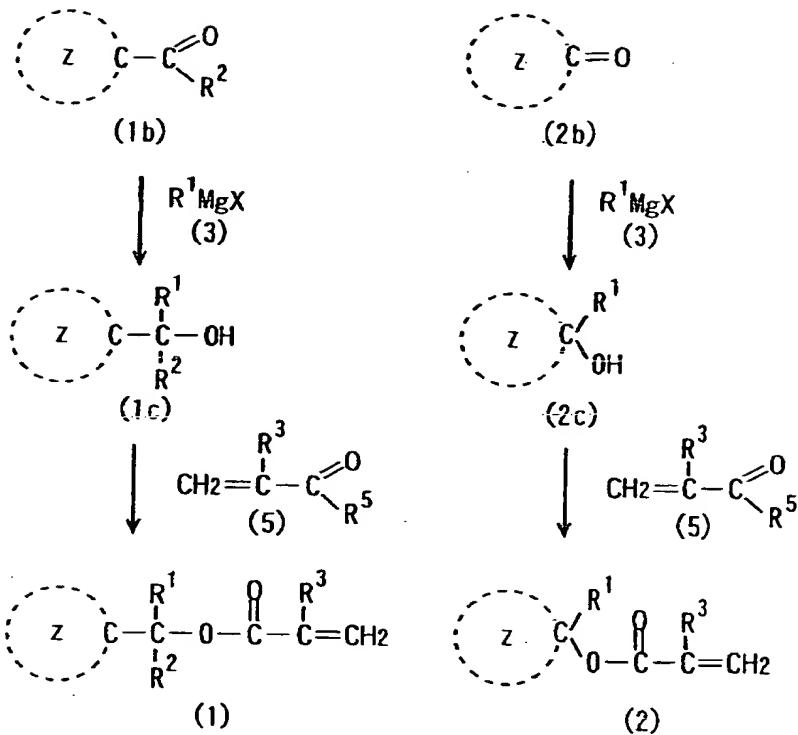


wherein R<sup>1a</sup> represents a C<sub>1-3</sub> alkyl group; R<sup>3</sup> represents hydrogen atom or methyl group; the Z<sup>a</sup> ring represents a bridged-ring alicyclic hydrocarbon ring which may have a substituent.

The acid-responsive compounds (1) and (2) of the present invention can be prepared in accordance with the following reaction schemes:

[0021]

[Formula 8]



wherein X represents halogen atom;  $\text{R}^5$  represents a halogen atom, hydroxyl group, an alkoxy group, an alkenyloxy group, or an alkynyloxy group; and  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ , and the ring Z have the same meanings as defined above.

The halogen atom typically includes chlorine, bromine and iodine, and the alkoxy group includes but is not limited to  $\text{C}_{1-10}$  alkoxy groups (e.g. methoxy, ethoxy, t-butoxy, etc.). The alkenyloxy group includes but is not limited to  $\text{C}_{2-10}$  alkenyloxy groups (e.g. vinyloxy, allyloxy, 1-propenyloxy, isopropenyloxy, 1-butenyloxy, 2-butenyloxy, 3-butenyloxy, 2-pentenyloxy, etc.), and the alkynyloxy group includes but is not limited to  $\text{C}_{2-10}$  alkynyloxy groups (e.g. ethynyloxy, propynyloxy, etc.).

[0022]

Referring to the above reaction schemes, the carbonyl compound (1b) includes, to mention typical examples, monocyclic compounds (cycloalkyl-1-C<sub>2-6</sub> alkanones such as cyclohexyl-1-ethanone etc.), spiro compounds (e.g. spiro[4.5]decan-8-yl-1-ethanone, spirobicyclohexan-9-yl-1-ethanone, etc.), ring assembly compounds (e.g. bicycloalkyl-1-C<sub>2-6</sub> alkanones such as bicyclohexan-4-yl-1-ethanone etc.), fused-ring compounds (e.g. perhydronaphthyl-1-ethanone, perhydrophenanthrenyl-1-ethanone, etc.), bridged-ring compounds (e.g. bicyclic compounds such as bornan-2-yl-1-ethanone, bornan-3-yl-1-ethanone, norbornan-2-yl-1-ethanone, etc. and tricyclic compounds such as adamantyl-1-C<sub>2-6</sub> alkanones, e.g. adamantan-1-yl-ethan-1-one, adamantan-1-yl-propan-1-one, adamantan-1-yl-butan-1-one, methyladamantan-1-yl-ethan-1-one, etc.); and derivatives from hydrogenated dimers of dienes (e.g. perhydro-4,7-methanoindenyl-1-C<sub>2-6</sub> alkanones such as perhydro-4,7-methanoinden-1-yl-1-ethanone etc.).

[0023]

The carbonyl compound (2b) includes but is not limited to monocyclic ketones (e.g. cycloalkanones such as cyclohexanone, methylcyclohexanone, etc.), spiro-ring ketones (spiro[4.5]decan-8-one, spirobicyclohexan-9-one, etc.), ring assembly ketones (e.g. bicycloalkanones such as bicyclohexan-4-one etc.), fused-ring compounds

(perhydronaphthalen-1-one, perhydronaphthalen-2-one, perhydrophenanthren-1-one, etc.), bridged-ring compounds (e.g. bicyclic compounds such as bornan-2-one, bornan-3-one, norbornan-2-one and tricyclic compounds such as adamantanone, methyladamantanone, dimethyladamantanone, etc.), and derivatives from hydrogenated dimers of dienes (e.g. perhydro-4,7-methanoinden-1-one etc.).

[0024]

In the above reaction schemes, the reaction of the carbonyl compound (1b) or (2b) with the reagent  $R^1MgX$  (3) can be carried out according to the conventional Grignard reaction. The amount of the Grignard reagent  $R^1MgX$  (3) relative to 1 mol of the carbonyl compound (1b) or (2b) may for example be about 0.8 to 3 mols, preferably about 1 to 2 mols, more preferably about 1 to 1.5 mols. This reaction can be conducted in an inert solvent to the reaction, such as hydrocarbons (hexane, cyclohexane, etc.), ethers (dimethyl ether, diethyl ether, tetrahydrofuran, etc.), to mention just a few preferred solvents. The reaction temperature can be suitably selected from the range of, for example, about 0 to 100°C, preferably about 10 to 50°C.

[0025]

The hydroxy compound (1c) or (2c) formed by the reaction, optionally isolated, is subjected to the esterification reaction using (meth)acrylic acid or a derivative thereof (5) to give the acid-responsive

compound (1) or (2).

[0026]

The (meth)acrylic acid or its derivative (5), mentioned above, includes (meth)acrylic acid, (meth)acrylic anhydride, and reactive derivatives having a leaving group [e.g. acid halides ((meth)acryloyl chloride, (meth)acryloyl bromide, etc.), (meth)acrylic acid alkyl esters such as C<sub>1-6</sub> alkyl (meth)acrylates (e.g. methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, etc.), (meth)acrylic acid alkenyl esters (e.g. C<sub>2-10</sub> alkenyl (meth)acrylates such as vinyl (meth)acrylate, allyl (meth)acrylate, 1-propenyl (meth)acrylate, isopropenyl (meth)acrylate, 1-butenyl (meth)acrylate, 2-butenyl (meth)acrylate, 3-butenyl (meth)acrylate, 2-pentenyl (meth)acrylate, etc.), and alkynyl esters of (meth)acrylic acid (e.g. C<sub>2-10</sub> alkynyl (meth)acrylates such as ethynyl (meth)acrylate, propynyl (meth)acrylate, etc.)].

The preferred compound (5) includes (meth)acrylic acid, (meth)acryloyl halides, C<sub>1-6</sub> lower alkyl esters of (meth)acrylic acid, C<sub>2-6</sub> alkenyl esters of (meth)acrylic acid, and C<sub>2-6</sub> alkynyl esters of (meth)acrylic acid. Particularly with a (meth)acryloyl halide or a C<sub>2-6</sub> alkenyl (meth)acrylate, the corresponding acid-responsive compound can be obtained with high selectivity and in high yield through a leaving group exchange reaction while side

reactions such as addition polymerization are inhibited.

[0027]

The above esterification reaction can be carried out by a conventional manner, for example in the presence of a suitable catalyst (an acid catalyst). When a (meth)acryloyl halide is used, there are cases in which the acid-responsive compound is contaminated with the halogen component. Therefore, this esterification reaction is preferably effected by the esterification reaction using (meth)acrylic acid or the transesterification reaction. The esterification reaction and transesterification reaction can be conducted using the conventional esterification catalyst (for example a non-halogen series inorganic acid such as sulfuric acid, hydrochloric acid, a sulfonic acid such as p-toluenesulfonic acid, a protonic acid such as acidic ion exchange resin, a Lewis acid such as boron trifluoride, an enzyme, etc.) and a transesterification catalyst (for example, the esterification catalysts, alkali metal alkoxide such as sodium alkoxides, aluminum alkoxides, titanic acid esters, etc.).

[0028]

To enhance the reaction efficiency and obtain the objective acid-responsive compound in high yield, the esterification reaction (inclusive of leaving group exchange reactions such as transesterification) between the hydroxy compound (1c) or (2c) and (meth)acrylic acid

or a derivative thereof (5) is conducted with advantage in the presence of a catalyst comprised of a compound of a Group 3 element of Periodic Table of the Elements. In the reaction utilizing such a catalyst, the formation of the amine hydrochloride can be inhibited and, when a C<sub>1-4</sub> lower alkyl ester or C<sub>2-4</sub> alkenyl ester of (meth)acrylic acid is used, the objective compound can be protected against contamination with the halogen component.

Moreover, because a low-boiling compound (e.g. the above ester) can be used as the (meth)acrylic acid or derivative (5), the treatment after the reaction is easy and the isolation yield can be dramatically increased.

[0029]

Referring to the catalyst comprised of a compound of Group 3 element, the Group 3 element includes rare earth elements, e.g. scandium, yttrium, lanthanide series elements (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium)], and actinoid series elements (e.g. actinium etc.). The preferred Group 3 element includes rare earth elements, such as scandium, yttrium, and lanthanoid series elements (samarium, gadolinium, ytterbium, etc.).

[0030]

The valence of the Group 3 element is not particularly restricted but is often bivalent to tetravalent, particularly bivalent or trivalent. The compound of Group

3 element, mentioned above, is not particularly restricted only if it has the necessary catalyst activity, and may be an elemental metal or a compound or complex of the metal with an inorganic compound (e.g. a halide, oxide, double oxide, phosphorus compound or nitrogen compound) or an organic compound (e.g. an organic acid). In many instances, it is the hydroxide or oxo-acid salt, organic acid salt, inorganic acid salt or halide containing the metal element or a coordination compound (complex) containing the metal element. The complex may be a  $\pi$  complex such as a metallocene compound. Furthermore, the compound of Group 3 element may be a double salt compound (complex metal compound) with another metal. Those catalysts can be used each alone or in a combination of two or more species.

[0031]

The catalyst component is now described in further detail taking a samarium compound as an example, it being, however, to be understood that the compounds of other Group 3 elements which correspond to the samarium compound can be used likewise with success.

The hydroxide includes samarium (II) hydroxide and samarium (III) hydroxide, for instance, and the metal oxide includes samarium (II) oxide and samarium (III) oxide, for instance.

The organic acid salt includes but is not limited to salts with such organic acids as organic carboxylic acids (monocarboxylic acids, polycarboxylic acids),

hydroxycarboxylic acids, thiocyanic acid or sulfonic acids (alkylsufonic acids, benzenesufonic acid, arylsulfonic acids, etc.). The inorganic acid salt includes but is not limited to the nitrate, sulfate, phosphate, carbonate and perchlorate. The organic acid salt and inorganic acid salt, mentioned above, include but are not limited to samarium acetate, samarium trichloroacetate, samarium trifluoroacetate, samarium trifluoromethanesulfonate (i.e. samarium triflate), samarium nitrate, samarium sulfate, samarium phosphate and samarium carbonate.

The halide may for example be the fluoride, chloride, bromide or iodide.

[0032]

The ligand forming the complex includes OH (hydroxo), alkoxy, acyl, alkoxy carbonyl, acetyl acetonato, cyclopentadienyl,  $C_{1-4}$  alkyl-substituted cyclopentadienyl (e.g.  $C_{1-2}$  alkyl-substituted cyclopentadienyl groups such as pentamethylcyclopentadienyl etc.), dicyclopentadienyl,  $C_{1-4}$  alkyl-substituted dicyclopentadienyl (e.g.  $C_{1-2}$  alkyl-substituted dicyclopentadienyl such as pentamethyldicyclopentadienyl etc.), halogen, CO, CN, oxygen,  $H_2O$  (aqua), phosphorus compounds such as phosphines, nitrogen-containing compounds such as  $NH_3$  (ammine), NO,  $NO_2$  (nitro),  $NO_3$  (nitrato), ethylenediamine, diethylenetriamine, pyridine, phenanthroline, etc. Referring to the complexes or complex salts, one or more similar or dissimilar ligands may be coordinated.

Among the complexes, samarocene complexes include diacetylacetonatosamarium (II), triacetylacetonatosamarium (III), dicyclopentadienylsamarium (II), tricyclopentadienylsamarium (III), dipentamethylcyclopentadienylsamarium (II) and tripentamethylcyclopentadienylsamarium (III).

[0033]

When the compound of Group 3 element [the bivalent samarocene complex having the pentamethylcyclopentadienyl ligands which are highly electron-donative  $[(C_5Me_5)_2Sm; (PMSm)]$  or any of samarium compounds such as samarium halides, alkoxide, hydroxide, etc.] is used as the catalyst, esterification proceeds with a higher efficiency and with side reactions inhibited as compared with the reaction in the presence of a Lewis acid catalyst or a protonic acid catalyst even in esterification reactions which are handicapped as equilibrium reactions. Thus, this catalyst is useful for producing the acid-responsive compounds (1) and (2) by a leaving group exchange reaction such as transesterification.

[0034]

The catalyst comprised of a compound of Group 3 element may be a homogeneous system or a heterogeneous system. Moreover, the catalyst may be an solid catalyst comprising the compound of Group 3 element supported on a support or carrier. The support is usually a porous

support such as activated carbon, zeolite, silica, silica-alumina, bentonite or the like. The amount of the supported catalyst component is about 0.1 to 50 parts by weight, preferably about 0.5 to 30 parts by weight, more preferably about 1 to 20 parts by weight relative to 100 parts by weight of the support.

[0035]

The amount of the catalyst (e.g. the catalyst comprised of the compound of Group 3 element) can be liberally selected from a broad range, for example the range of about 0.1 mol % to 1 equivalent, preferably about 0.5 to 50 mol %, more preferably about 1 to 25 mol % (e.g. about 5 to 20 mol %), based on the hydroxy compound (1c) or (2c).

[0036]

The esterification reaction mentioned above (particularly the reaction using the compound of Group 3 element as the catalyst) may be conducted in the presence of an oxime. The oxime may be whichever of an aldoxime or a ketoxime and includes aliphatic oximes such as 2-hexanone oxime etc., alicyclic oximes such as cyclohexanone oxime etc., and aromatic oximes such as acetophenone oxime, benzophenone oxime, benzyl dioxime, etc.

The amount of the oxime can be selected from a broad range, for example the range of about 0.1 mol % to 1 equivalent, preferably about 1 to 50 mol %, more preferably about 5 to 40 mol % (e.g. about 5 to 30 mol %), based on the hydroxy compound (1c) or (2c).

[0037]

The ratio of (meth)acrylic acid or its derivative (5) to hydroxy compound (1c) or (2c) is about 0.5 to 5 mols, preferably about 0.8 to 5 mols, more preferably not less than 1 mol (e.g. about 1 to 3 mols, particularly about 1 to 1.5 mols) of (meth)acrylic acid or derivative (5) per equivalent of hydroxy compound (1c) or (2c) (that is the weight of the hydroxy compound per hydroxyl group). Since the esterification reaction is an equilibrium-controlled reaction, it is more advantageous to use a larger proportion of (meth)acrylic acid or derivative thereof (5) for accelerating the reaction but because of the usually high catalyst activity of the compound of Group 3 element, (meth)acrylic acid or derivative thereof (5) need not be used in a large excess. Particularly, in the reaction involving a combination of reactants which is very unfavorable from the standpoint of reaction equilibrium, the use of the alkenyl ester having a vinyl leaving group (e.g. vinyl ester) as the (meth)acrylic acid or derivative thereof (5) rather leads, in many instances, to an early completion of reaction and a better result even if the compound (1c) is used in a proportion of only 1 mol or less (e.g. 0.4 to 1 mol, particularly 0.5 to 1 mol) per equivalent of the leaving group of hydroxy compound (1c) or (2c).

In the process using the catalyst, the heat of reaction is not so high as in the process using an acid halide such as (meth)acryloyl chloride so that the reaction

can be smoothly conducted in a small amount of solvent and the end product can be obtained in a higher yield.

[0038]

The esterification reaction mentioned above can be carried out in the presence or absence of a solvent inert to the reaction. The reaction solvent which can be used includes but is not limited to aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, polar aprotic solvents such as ketones, ethers, amides, N-methylpyrrolidone, nitriles, etc. and mixed solvents thereof. As the reaction solvent, (meth)acrylic acid or derivative thereof (5) may be used.

When a highly hydrophilic species of hydroxy compound (1c) or (2c) is used, the solvent may be a hydrophilic solvent (ketones such as acetone, methyl ethyl ketone, etc., ethers such as dioxane, diethyl ether, tetrahydrofuran, etc., and other polar aprotic solvents), or a mixed solvent of a hydrophilic solvent and a hydrophobic solvent (an aliphatic, alicyclic or aromatic hydrocarbon).

[0039]

Since the above reaction is an equilibrium-controlled reaction, it is advantageous to remove the reaction-interfering components such as the cleaved (eliminated) component from the reaction system for accelerating the reaction. For removal of the eliminated component, it is advantageous to use a high-boiling solvent (for example an organic solvent boiling at 50 to 120°C,

particularly about 60 to 115°C) or an azeotropic solvent (for example the hydrocarbons).

[0040]

The esterification reaction temperature can be selected from the range of, for example, about 0 to 150°C, preferably about 25 to 120°C. When the catalyst comprised of the compound of Group 3 element is used, the acid-responsive compound forms with high efficiency even under mild conditions. Thus, the reaction temperature may for example be about 0 to 150°C, preferably about 10 to 100°C, more preferably about 20 to 80°C. Particularly when the alkenyl ester, for instance, is used as the (meth)acrylic acid or derivative (5), the reaction can be smoothly carried through even under mild conditions, namely at about 20 to 50°C. The reaction can be conducted at atmospheric pressure, under applied pressure or at elevated pressure. Moreover, the reaction can be carried out batchwise, semi-batchwise or continuously in the conventional manner.

[0041]

After completion of the reaction, the acid-responsive compound (1) or (2) can be easily isolated and purified by such separatory means as filtration, concentration, distillation, extraction, crystallization, recrystallization, column chromatography, etc. as applied independently or in combination.

[0042]

[Photoresist resin composition]

The photoresist resin composition of this invention is characterized in that at least a polymer containing the unit of formula (11) or (12) (e.g. a unit having an adamantane skeleton) and a photoactive acid precursor (photoactive acid generator) are used in combination and that the polymer is solubilized by irradiation with light. Thus, probably because the branched-chain alkyl group containing a tertiary carbon atom is adjacent to the bulky, hydrophobic ring Z and the ester bond is stably eliminated with high efficiency by the acid produced by the irradiation, a fine-line resist pattern can be formed with high accuracy and reproducibility while the high sensitivity and high etching resistance are maintained.

[0043]

The polymer mentioned above may be a homopolymer or a copolymer of the acid-responsive compound or compounds represented by formula (1) or/and (2) or a copolymer of the acid-responsive compound or compounds of formula (1) or/and (2) with one or more other copolymerizable monomers.

The copolymerizable monomers mentioned above include but are not limited to (meth)acrylic monomers (e.g. (meth)acrylic  $C_{1-10}$  alkyl esters such as methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, s-butyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, etc.; (meth)acrylic hydroxy  $C_{2-6}$  alkyl

esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, etc.; glycidyl (meth)acrylate, (meth)acrylonitrile, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, etc.), styrenic monomers (styrene,  $\alpha$ -methylstyrene, vinyltoluene, etc.), vinyl ester monomers (vinyl acetate, vinyl propionate, etc.), carboxyl group-containing monomers ((meth)acrylic acid, maleic anhydride, itaconic acid, maleic monoesters, etc.), sulfonic acid group-containing monomers (styrenesulfonic acid etc.).

[0044]

The proportion of the acid-responsive compound (1), (2) in the copolymer may for example be about 10 to 100 weight % (e.g. 15 to 90 weight %), preferably about 25 to 100 weight % (e.g. 30 to 75 weight %), more preferably about 30 to 100 weight % (e.g. 35 to 70 weight %).

[0045]

The photoactive acid precursor which can be used includes the conventional compounds which, when exposed to light, form acids (protic acids or Lewis acids) with high efficiency, for example diazonium salts, iodonium salts, sulfonium salts, oxathiazole derivatives, s-triazine derivatives, imide compounds, oxime sulfonates, diazonaphthoquinone, sulfonic esters [1-phenyl-1-(4-methylphenyl)sulfonyloxy-1-benzoylmethane, 1,2,3-trisulfonyloxyethylbenzene, 1,3-dinitro-2-(4-phenylsulfonyloxyethyl)benzene, 1-phenyl-1-(4-

methylphenyl)sulfonyloxyethyl-1-hydroxy-1-benzoymethane, disulfone derivatives (diphenyl disulfone etc.), benzoin tosylate, etc.] or Lewis acids (triphenylsulfonium hexafluoroantimonate  $((\text{Ph})_3\text{S}^+\text{SbF}_6^-)$ , triphenylsulfonium hexafluorophosphate  $((\text{Ph})_3\text{S}^+\text{PF}_6^-)$ , triphenylsulfonium methanesulfonyl  $((\text{Ph})_3\text{S}^+\text{CH}_3\text{SO}_3^-)$ , diphenyliodonium hexafluorophosphate, etc.). In the above description, Ph represents a phenyl group.

Those photoactive acid precursors can be used each alone or in a combination of two or more species.

[0046]

The amount of the photoactive acid precursor can be selected according to the strength of the acid that will be produced by irradiation and the amount of the acid-responsive compound, among other conditions, for example from the range of about 0.1 to 30 parts by weight, preferably about 1 to 25 parts by weight, more preferably about 2 to 20 parts by weight, relative to 100 parts by weight of the polymer.

[0047]

The photoresist resin composition may contain an alkali-soluble component such as alkali-soluble resin (novolac resin, phenolic resin, carboxyl-containing resin, etc.), a coloring agent (dye), an organic solvent, etc. The organic solvent includes but is not limited to hydrocarbons, halogenated hydrocarbons, alcohols, esters, ketones, ethers, cellosolves, carbitols, glycol ether

esters (cellosolve acetates) and mixed solvents thereof.

Further, the photoresist resin composition may be free of contaminants by the conventional separation and purification procedure such as the use of a filter.

[0048]

The photoresist resin composition of this invention can be prepared by mixing the polymer and the photoactive acid precursor. After this photoresist resin composition is coated on a substrate or base and dried, and the resulting layer (resist film) is exposed to light through a given mask to form a latent pattern and then developed, providing a fine-line pattern with high accuracy. The sensitivity to light and pattern resolution are high.

[0049]

The substrate or base can be selected according to the intended use of the photoresist resin composition and may for example be a silicon wafer or a metal, plastic, glass, ceramic or other substrate. The coating with the photoresist resin composition can be effected by the conventional procedure suited to each application, for example by the spin coating technique or the roll coating technique. The thickness of coating layer comprising the photoresist resin composition can be judiciously selected from the range of, for example, about 0.1 to 20  $\mu\text{m}$ .

[0050]

For the exposure to light, light beams of various wavelengths, e.g. ultraviolet rays and X-rays, can be

employed. For the exposure of resists for semiconductor manufacturing, g-line, i-line, and excimer laser (e.g. XeCl, KrF, KrCl, ArF, ArCl, etc.) beams can be utilized.

The exposure beam energy can be selected from the range of, for example, about 1 to 1000 mJ/cm<sup>2</sup>, preferably about 10 to 500 mJ/cm<sup>2</sup>.

[0051]

On irradiation, an acid is generated from the acid precursor and the group containing the Z ring (usually the alcohol containing the Z ring) is eliminated by the generated acid and a carboxyl group contributory to solubilization is generated. Therefore, the desired pattern can be formed using an aqueous developer or an alkali developer. Particularly because the photoresist resin composition of the present invention has the Z ring, such as an adamantane skeleton, it is highly resistant to etching (dry etching in particular) so that an elaborate circuit pattern can be formed with high accuracy. Incidentally, the cleavage of the group containing the Z ring may be promoted by exposure and post-exposure baking (PEB).

The present invention can be embodied in various applications, such as circuit-forming materials (resists for semiconductor manufacturing, printed circuit boards, etc.) and image-forming materials (printing plates, relief images, etc.).

[0052]

[Introduction of functional groups]

The acid-responsive compounds (1) and (2) and the polymer component units (11) and (12) have the substituent  $R^4$  as mentioned above. The substituent  $R^4$  can be introduced in a suitable stage among the above-described reaction stages or after completion of the relevant reaction. The hydroxyl group, for instance, can be given by a conventional oxidation process using nitric acid or chromic acid, an oxidation process using oxygen with a cobalt salt as the catalyst or a biochemical oxidation process, for instance, or generated by a method which comprises introducing a halogen atom (e.g. a bromine atom) and then carrying out a hydrolysis reaction using an inorganic salt such as silver nitrate or silver sulfate to thereby introduce a hydroxyl group. As a preferred method, the method using an oxidation catalyst as described in Japanese Patent Application Laid-Open No.327626/1997, for instance, can be mentioned. In this oxidation method, the substrate compound of formula (1a), (2a), (1b), (2b), (1c) or (2c) or the polymer component unit (11) or (12) can be oxidized with oxygen in the presence of an oxidation catalyst comprised of a certain imide compound or an oxidation catalyst comprised of the imide compound and a co-catalyst to thereby introduce a hydroxyl group.

[0053]

The imide compound mentioned above includes compounds having N-hydroxyimide groups (e.g. aliphatic, alicyclic and aromatic compounds each having about 1 to

3 N-hydroxyimido groups), such as N-hydroxysuccinimide, N-hydroxymaleimide, N-hydroxyhexahydrophthalimide, N,N'-dihydroxycyclohexanetetracarboximide, N-hydroxyphthalimide, N-hydroxytetrabromophthalimide, N-hydroxytetrachlorophthalimide, N-hydroxyhetimide, N-hydroxyhimimide, N-hydroxytrimellitimide, N,N'-dihydroxypyromellitimide, and N,N'-dihydroxynaphthalenetetracarboximide. Among the preferred compounds are N-hydroxyimide compounds derived from alicyclic polycarboxylic anhydrides, particularly those derived from aromatic polycarboxylic anhydrides, for example N-hydroxyphthalimide.

[0054]

Such imide compounds have high oxidizing activity and are capable of promoting an oxidation reaction catalytically even under mild condition. Furthermore, by oxidizing a substrate in the presence of the imide compound and a co-catalyst, a hydroxyl group can be introduced with high efficiency.

[0055]

The co-catalyst includes metal compounds, for example compounds containing elements of Group 2A of Periodic Table of the Elements, transition metal elements (e.g. Group 3A elements, Group 4A elements, Group 5A elements, Group 6A elements, Group 7A elements, Group 8 elements, Group 1B elements, and Group 2B elements) and elements of Group 3B (boron B, aluminum Al, etc.) of the

Periodic Table of Elements.

[0056]

The co-catalyst may for example be an elemental metal or a hydroxide thereof but, in many instances, metal oxides (double oxides or oxo-acid salts), organic acid salts, inorganic acid salts and halides containing the elements, coordination compounds (complexes) and polyacids (heteropolyacids and isopolyacids) or their salts containing the metal elements are used.

[0057]

The oxidation catalyst comprised of the imide compound or the oxidation catalyst comprising the imide compound and co-catalyst may be a homogeneous system or a heterogeneous system. Moreover, the oxidation catalyst or oxidation catalyst system may be a solid catalyst comprising a catalytic component supported on a support or carrier.

[0058]

The ratio of the co-catalyst to the imide compound can be selected from the range of, for example, about 0.001 to 10 mols of the co-catalyst relative to 1 mol of the imide compound. In order to maintain the activity level of the oxidation catalyst system high, the amount of the co-catalyst is preferably from an effective amount to 0.1 mol (for example, about 0.001 to 0.1 mol, preferably about 0.005 to 0.08 mol, more preferably about 0.01 to 0.07 mol) relative to 1 mol of the imide compound.

[0059]

The amount of the imide compound relative to 1 mol of the substrate is about 0.001 to 1 mol (0.01 to 100 mol %), preferably about 0.001 to 0.5 mol (0.1 to 50 mol %), more preferably about 0.01 to 0.30 mol.

The amount of the co-catalyst relative to 1 mol of the substrate is about 0.0001 mol (0.1 mol %) to 0.5 mol, preferably about 0.001 to 0.3 mol, more preferably about 0.0005 to 0.1 mol (e.g. 0.005 to 0.1 mol), in many instances.

The oxygen for use in the oxidation reaction may be active oxygen but it is economically advantageous to use molecular oxygen. The molecular oxygen is not particularly restricted but may be pure oxygen or oxygen diluted with an inert gas such as nitrogen, helium, argon or carbon dioxide. Not only from the standpoint of workability (handling easiness) and safety but also from economic points of view, the use of air is preferable.

The amount of oxygen relative to 1 mol of the substrate is usually not less than about 0.5 mol (e.g. 1 mol or more), preferably about 1 to 100 mols, more preferably about 2 to 50 mols. Oxygen is often used in excess mol relative to the substrate and it is particularly advantageous to carry out the reaction in an atmosphere containing molecular oxygen such as air or oxygen gas.

[0060]

The oxidation reaction is usually carried out in an organic solvent inert to the reaction. The organic solvent

that can be used includes but is not limited to organic carboxylic acids such as acetic acid and hydroxycarboxylic acids, nitriles such as acetonitrile, benzonitrile, etc., amides such as formamide, acetamide, dimethylformamide (DMF), dimethylacetamide, etc., alcohols such as t-butanol, t-amyl alcohol, etc., aliphatic hydrocarbons such as hexane, octane, etc., aromatic hydrocarbons such as benzene etc., halogenated hydrocarbons, nitro compounds, esters such as ethyl acetate etc., ethers such as diethyl ether, diisopropyl ether, dioxane, etc., and mixed solvents thereof.

[0061]

When the oxidation reaction is carried out in the presence of a protonic acid, the reaction proceeds smoothly and the objective compound can be obtained with high selectivity and in good yield. The protonic acid may be utilized as the solvent as mentioned above. The protonic acid includes organic acids (e.g. organic carboxylic acids such as formic acid, acetic acid, propionic acid, etc., oxalic acid, hydroxycarboxylic acids such as citric acid, tartaric acid, etc., alkylsulfonic acids such as methanesulfonic acid, ethanesulfonic acid, etc., arylsulfonic acids such as benzenesulfonic acid, p-toluenesulfonic acid, etc.) and inorganic acids (e.g. hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, etc.).

[0062]

The oxidation method using the oxidation catalyst or oxidation catalyst system is characterized in that the oxidation reaction proceeds smoothly even under comparatively mild conditions. The reaction temperature may for example be about 0 to 200°C, preferably about 30 to 150°C, and the reaction is generally conducted at about 50 to 120°C in many instances. This reaction can be conducted at atmospheric or under applied pressure.

When the above oxidation reaction is carried out in the presence of a strong acid, an oxo group can be introduced with high efficiency. The strong acid includes not only sulfuric acid and sulfonic acids mentioned above but also superacids, among others.

[0063]

The introduction of a carboxyl group can be achieved by various reactions but it is advantageous to employ a technique (carboxylation process) similar to the above-described oxidation reaction process using the imide compound (or the imide compound and co-catalyst) as a catalyst except that carbon monoxide and oxygen are used in lieu of oxygen. The carbon monoxide and oxygen may be pure carbon monoxide and oxygen or carbon monoxide and oxygen as diluted with an inert gas beforehand in the same manner as mentioned for the oxidation reaction. As the oxygen source, air may be likewise employed.

[0064]

The proportion of carbon monoxide can be selected

from the range of not less than 1 mol (e.g. 1 to 1000 mols) relative to 1 mol of the substrate and is preferably an excess mole, for example about 1.5 to 100 mols (e.g. 2 to 50 mols), more preferably about 2 to 30 mols (e.g. 5 to 25 mols).

The proportion of oxygen relative to 1 mol of the substrate can be selected from the range of not less than 0.5 mol (e.g. 0.5 to 100 mols), preferably about 0.5 to 30 mols, more preferably about 0.5 to 25 mols.

[0065]

It is preferable to use a larger amount of carbon monoxide than oxygen. The usual ratio of CO to O<sub>2</sub> is CO/O<sub>2</sub> = about 1/99 to 99/1 (mol %) [e.g. 10/90 to 99/1 (mol %)], preferably about 30/70 to 98/2 (mol %), more preferably about 50/50 to 95/5 (mol %), particularly about 60/40 to 90/10 (mol %).

A hydroxymethyl group can be generated by reducing the carboxyl group-introduced substrate with hydrogen or a hydrogenation reducing agent (e.g. sodium boron hydride-Lewis acid, aluminum hydride, lithium aluminum hydride, lithium trialkoxyaluminum hydrides, diborane, etc.).

[0066]

A nitro group can be introduced in the conventional manner, for example by a process using a nitrating agent (e.g. mixed acid of sulfuric acid and nitric acid; nitric acid; nitric acid and an organic acid (e.g. a carboxylic

acid such as acetic acid); a nitrate and sulfuric acid; dinitrogen pentoxide, etc.).

The preferred nitration process may for example be a nitration process which comprises contacting the substrate with a nitrogen oxide in the presence or absence of the imide compound (or the imide compound and co-catalyst).

[0067]

The nitrogen oxide mentioned above can be expressed by the formula  $N_xO_y$  (wherein x represents an integer of 1 or 2; y represents an integer of 1 to 6).

In the compound of the above formula, when x is equal to 1, y is usually an integer of 1 to 3 and when x is equal to 2, y is usually an integer of 1 to 6.

[0068]

The nitrogen oxide, thus, includes but is not limited to  $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_4$ ,  $N_2O_5$ ,  $NO_3$  and  $N_2O_6$ . Those nitrogen oxides can be used each independently or in a combination of two or more species.

[0069]

The preferred nitrogen oxide includes (1) the nitrogen oxide (particularly  $N_2O_3$ ) produced by reacting at least one nitrogen compound selected from the group consisting of dinitrogen oxide ( $N_2O$ ) and nitrogen monoxide ( $NO$ ) with oxygen or a nitrogen oxide containing  $N_2O_3$  as a main component and (2) nitrogen dioxide ( $NO_2$ ) or a nitrogen oxide containing  $NO_2$  as a main component.

The nitrogen oxide  $N_2O_3$  can be easily obtained by reacting  $N_2O$  and/or NO with oxygen. More specifically, it can be prepared by a process which comprises charging a reactor with nitrogen monoxide and oxygen to give  $N_2O_3$  as a blue-colored liquid. Therefore, instead of preparing  $N_2O_3$  in advance, the nitration reaction may be carried out by introducing  $N_2O$  and/or NO and oxygen into the reaction system.

Here, the oxygen may be either pure oxygen or oxygen diluted with an inert gas (carbon dioxide, nitrogen, helium, argon, etc.) beforehand. The oxygen source may be air.

[0070]

In the reaction mode using nitrogen dioxide ( $NO_2$ ), among the nitrogen oxides, the nitration reaction proceeds smoothly even without coexistence of oxygen. Therefore, the reaction system using  $NO_2$  does not essentially require oxygen, although  $NO_2$  may be used in combination with oxygen.

[0071]

In the above oxidation process using the imide compound (or the imide compound and co-catalyst) as a catalyst, it is advantageous to carry out nitration using a nitrogen oxide (or a nitrogen oxide and oxygen) in lieu of oxygen in otherwise the same manner as the oxidation process described above.

[0072]

The amount of the nitrogen oxide can be selected according to the amount of the nitro group to be introduced,

for example from the range of about 1 to 50 mols, preferably about 1.5 to 30 mols, relative to 1 mol of the substrate, and is usually about 2 to 25 mols.

[0073]

When the catalyst comprised of the imide compound is used, the nitration reaction proceeds smoothly even under comparatively mild conditions. The reaction temperature can be selected according to the kinds of imide compound and substrate, for example from the range of about 0 to 150°C, preferably about 25 to 125°C, more preferably about 30 to 100°C. The nitration reaction can be carried out at atmospheric pressure or under applied pressure.

[0074]

The nitro-group introduced into the substrate can be converted to an amino group by reduction. The reduction reaction can be carried out according to a conventional method, for example by catalytic hydrogenation using hydrogen as the reducing agent or by the reduction reaction using a hydrogenation reducing agent.

The catalyst for the catalytic hydrogenation includes but is not limited to elemental metals (simple metals) such as platinum, palladium, nickel, cobalt, iron and copper and compounds containing such metal elements (e.g. platinum oxide, palladium black, palladium-carbon, copper chromite, etc.). The amount of the catalyst is generally about 0.02 to 1 mol relative to 1 mol of the adamantane (substrate). The reaction temperature for

catalytic hydrogenation may for example be about -20°C to 100°C (e.g. 0 to 70°C). The hydrogen pressure is generally 1 to 10 atmospheres in many instances.

[0075]

Referring to the reduction reaction using a hydrogenation reducing agent, the hydrogenation reducing agent which can be used includes but is not limited to aluminum hydride, sodium boron hydride, and diborane. The amount of the hydrogenation reducing agent used relative to 1 mol of the substrate is generally not less than 1 mol (for example, about 1 to 10 mols) in many instances. In many cases of reduction using a hydrogenation reducing agent, the reaction temperature is generally about 0 to 200°C (for example 0 to 170°C).

The above reduction reaction (catalytic hydrogenation method, the process using a hydrogenation reducing agent) may be carried out in a solvent inert to the reduction reaction (the solvents exemplified in the item of the oxidizing reaction, for example, carboxylic acids, ethers, esters and amides).

[0076]

The hydroxyl group introduced into the substrate can be converted to an alkoxy group in the routine manner, and the carboxyl group can be converted to an alkoxy carbonyl group, a carbamoyl group or an N-substituted carbamoyl group by utilizing the conventional esterification reaction or amidation reaction, for instance. Furthermore,

the amino group can be converted to an N-substituted amino group using an alkylating agent or an acylating agent.

[0077]

The compound and polymer having a basic group or an acidic group may form salts. For example, a carboxyl group-containing substrate can be reacted with an organic base or an inorganic base to give the corresponding salt. An amino group-containing substrate can be reacted with an inorganic acid or an organic acid to give the corresponding salt.

[0078]

The oxidation and other reactions can be carried out in any of batch, semi-batch and continuous modes. After completion of each reaction, the reaction product can be easily isolated and purified by the conventional procedure.

[0079]

[Effects of the Invention]

The acid-responsive compound of the present invention has an alicyclic hydrocarbon group (e.g. an adamantine skeleton) and becomes alkali-soluble upon exposure to light, with the result that it finds application as a photoresist in the formation of fine-line patterns. Furthermore, because it is high in sensitivity and etching resistance (dry etching resistance in particular), fine-line patterns can be formed with good reproducibility and high accuracy. In addition, it contributes to improved

adhesion to the substrate and improved stability of the resist solution, thus insuring the formation of fine-line patterns with high accuracy and good reproducibility.

[0080]

[Examples]

Hereinafter, the present invention will be described in further detail with reference to Examples and Comparative Examples but should by no means be construed as defining the present invention.

Example 1

(1) Hydroxylation

To a solution of adamantan-1-yl-ethan-1-one (1 mol) in absolute tetrahydrofuran was added a solution of isopropylmagnesium iodide (iso-C<sub>3</sub>H<sub>7</sub>MgI) (1.2 mols) in absolute diethyl ether dropwise, and the mixture was stirred at 10°C for 6 hours to provide 1-(2-hydroxyisopentyl)adamantane.

(2) Esterification

A mixture of 1-(2-hydroxyisopentyl)adamantane obtained above (1.00 mmol), samarium iodide (SmI<sub>2</sub>) (0.10 mmol), isopropenyl acrylate (1.1 mmols) and dioxane (2 mmols) was stirred at 50°C for 6 hours. Analysis by gas chromatography revealed the formation of 1-(2-acryloyloxyisopentyl)adamantane (yield 90%) in the reaction mixture.

Mass spectrum: [M] 276, 261, 246, 231, 218, 191, 147.

(3) Polymerization

A monomer mixture (100 parts by weight) of the

obtained 1-(2-acryloyloxyisopentyl)adamantane (50 weight %), methyl methacrylate (10 weight %), butyl acrylate (20 weight %) and methacrylic acid (20 weight %) was polymerized in an organic solvent (toluene) in the presence of polymerization initiator (benzoyl peroxide) (5 parts by weight), and the polymer was precipitated by adding methanol to the reaction mixture. The precipitate was purified by repeating the cycle of dissolution in toluene and precipitation with methanol to provide a copolymer having a weight average molecular weight of about  $1.5 \times 10^4$  (molecular weight in terms of polystyrene according to GPC).

[0081]

Example 2

(1) Hydroxylation

A mixture of 1-(2-acryloyloxyisopentyl)adamantane (10 mmols), NHPI (2 mmols), acetylacetonecobalt ( $\text{Co}(\text{AA})_2$ ) (0.1 mmol) and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6 hours to provide 1-hydroxy-5-(2-acryloyloxyisopentyl)adamantane (yield 78%).

Mass spectrum of hydroxyl group-containing compound:

[M] 292, 274, 259, 244, 229, 216, 189, 145.

(2) Polymerization

Using 1-hydroxy-5-(2-acryloyloxyisopentyl)adamantane in lieu of 1-(2-acryloyloxyisopentyl)adamantane, Step (3) of Example 1 was

otherwise repeated to provide a copolymer.

[0082]

Example 3

(1) Introduction of a carboxyl group

To acetic acid (25 ml) were added adamantan-1-yl-ethan-1-one (10 mmols), NHPI (1 mmol) and Co(AA)<sub>2</sub> (0.005 mmol), and the mixture was stirred at 60°C for 6 hours in a reactor with a gas pack inflated with a mixed gas (a mixed gas of carbon monoxide (2 L) and oxygen (0.5 L); pressure: 5 kg/cm<sup>2</sup>). As a result, 1-carboxyadamantan-5-yl-ethan-1-one was obtained at a conversion rate of 78% (yield 62%).

Using 1-carboxyadamantan-5-yl-ethan-1-one in lieu of adamantan-1-yl-ethan-1-one, Step (1) of Example 1 was otherwise repeated to provide 1-carboxy-5-(2-hydroxy-2-isopentyl)adamantane (yield 60%).

[0083]

(2) (3) Esterification and polymerization

Using 1-carboxy-5-(2-hydroxy-2-isopentyl)adamantane in lieu of 1-(2-hydroxyisopentyl)adamantane, Steps (2) and (3) of Example 1 were otherwise repeated to provide the carboxyl group-containing compound, namely 1-carboxy-5-(2-acryloyloxy-2-isopentyl)adamantane (yield 82%), and a copolymer.

[0084]

Mass spectrum of carboxyl group-containing compound: [M] 320, 249, 234, 219, 204, 191, 179, 134

Example 4

(1) Hydroxylation

Using adamantanone in lieu of adamantan-1-yl-ethan-1-one, Step (1) of Example 1 was otherwise repeated to provide 2-isopropyl-2-hydroxyadamantane at a conversion of 76% (yield 61%).

[0085]

(2), (3) Esterification and polymerization

Using 2-isopropyl-2-hydroxyadamantane in lieu of 1-(2-hydroxyisopentyl)adamantane, Steps (2), (3) of Example 1 were otherwise repeated to provide a hydroxyl group-containing compound, namely 2-isopropyl-2-acryloyloxyadamantane (yield 78%), and a copolymer.

Mass spectrum of hydroxyl group-containing compound: [M] 248, 233, 218, 205, 183, 139.

[0086]

Example 5

(1) Hydroxylation

Using 2-isopropyl-2-acryloyloxyadamantane in lieu of 1-(2-acryloyloxyisopentyl)adamantane, the hydroxylation step (Step 2) of Example 2 was otherwise repeated to provide 1-hydroxy-4-isopropyl-4-acryloyloxyadamantane (yield 56%).

Mass spectrum of hydroxyl group-containing compound: [M] 264, 246, 231, 216, 203, 176, 132.

(2) Polymerization

Using 1-hydroxy-4-isopropyl-4-acryloyloxyadamantane in lieu of 1-(2-

acryloyloxyisopentyl)adamantane, Step (3) of Example 1 was otherwise repeated to provide a copolymer.

[0087]

Example 6

(1) Introduction of a carboxyl group

Using adamantanone in lieu of adamantan-1-yl-ethan-1-one, the carboxylation step (Step 1) of Example 3 was otherwise repeated to provide 1-carboxyadamantan-4-one.

Using 1-carboxyadamantan-4-one in lieu of adamantan-1-yl-ethan-1-one, Step (1) of Example 1 was otherwise repeated to provide 1-carboxy-4-(2-hydroxy-2-isopentyl)adamantane (yield 58%).

[0088]

(2), (3) Esterification and polymerization

Using 1-carboxy-4-(2-hydroxy-2-isopentyl)adamantane in lieu of 1-(2-hydroxyisopentyl)adamantane, Steps (2) and (3) of Example 1 were otherwise repeated to provide a carboxyl group-containing compound, namely 1-carboxy-4-(2-acryloyloxy-2-isopentyl)adamantane (yield 81%), and a copolymer.

[0089]

Mass spectrum of carboxyl group-containing compound: [M] 292, 221, 206, 191, 178, 133

[Photoresist resin composition]

A photoresist resin composition was prepared by

mixing 100 parts by weight of each polymer obtained and 15 parts by weight of triphenylphosphoniumhexafluoroantimony with the solvent toluene. This photoresist resin composition was coated on a silicon wafer by the spin coating technique to form a 1.0  $\mu\text{m}$  thick photosensitive layer. After prebaking on a hot plate at 60°C for 100 seconds, exposure was carried out at an illuminating amount 100  $\text{mJ}/\text{cm}^2$  using a KrF excimer stepper, followed by postbaking at 100°C for 60 seconds. Development was then carried out with an aqueous alkaline solution (Tokyo Oka K.K., NMD-3) for 60 seconds and the wafer was rinsed with pure water. As a result, a predetermined pattern could be formed.

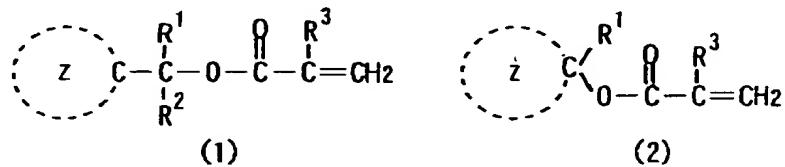
[ Document Name ] ABSTRACT

### [Abstract]

[Object] To provide a photoresist resin composition high in etching resistance, solubilizable by irradiation, and capable of forming a finer line pattern.

[Means to Solve the Problems] The photoresist resin composition comprises a polymer containing an acid-responsive compound unit of the following formula (e.g. an adamantane skeleton) and a photoactive acid precursor.  $R^1$  usually has a tertiary carbon atom in the 1-position and the ring Z is a bridged-ring hydrocarbon ring comprising 2 to 4 rings.

[Formula 1]



wherein R<sup>1</sup> represents a branched-chain alkyl group having a tertiary carbon atom; R<sup>2</sup> represents hydrogen atom or an alkyl group; R<sup>3</sup> represents hydrogen atom or methyl group; the Z ring represents a monocyclic or polycyclic alicyclic hydrocarbon ring which may have a substituent.

[ Selected Fig. ] none

[Document Name] Official Correction Data  
[Corrected Document] Petition of Patent

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Identification No. [000002901]

1. Date of Alteration August 28, 1990

[Reason of Alteration] new registration

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DECLARATION

I, Maemi NAKANISHI, declare that I reside at 38-1-A106,  
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That I am familiar with the English and Japanese  
languages;

That I have prepared a translation of Japanese Patent  
Application No. 244067/1998, "酸感応性化合物及びフォトレジスト用  
樹脂組成物, ACID-RESPONSIVE COMPOUNDS AND RESIN COMPOSITIONS  
FOR PHOTORESIST"; said translation thereof being attached  
hereto and made a part of this declaration;

That to the best of my knowledge and belief, the attached  
translation is accurate and fairly reflects the contents and  
meaning of the foregoing Japanese language document.

I declare, under penalty of perjury under the laws of  
the United States of America, that the foregoing is true and  
correct.

Executed, on August 30, 2001.

Maemi Nakanishi

Maemi NAKANISHI

PATENT OFFICE

JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy  
of the following application as filed with this Office.

Date of Application: August 28, 1998

Application Number: 244067/1998

Applicant(s): Daicel Chemical Industries, Ltd.

June 11, 1999

Commissioner,

Patent Office

Takeshi ISAYAMA

Certification No. 3037509/1999

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[Docket No.] P980096  
[Filing Date] August 28, 1998  
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Office  
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Classification C01L 21/027  
[Title of the Invention] ACID-RESPONSIVE COMPOUNDS  
AND RESIN COMPOSITIONS FOR  
PHOTORESIST  
[The number of Claims] 9  
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[Application No.] 143536/1998

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[Payment of Fees]

[Payment Book No.] 009829

[Amount to be paid] ¥21,000

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[Item] Specification one copy

[Item] Abstract one copy

[Identification No. of General Power] 9001562

[Requirement of Proof] Yes

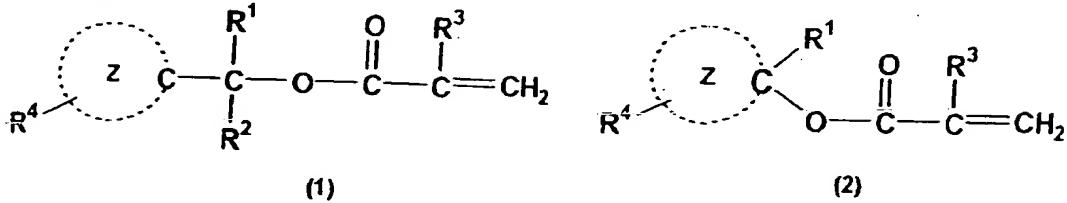
[Document Name] SPECIFICATION

[Title of the Invention] ACID-RESPONSIVE COMPOUNDS AND RESIN COMPOSITIONS FOR PHOTORESIST

[Claims]

[Claim 1] An acid-responsive compound represented by the following formula (1) or (2)

[Formula 1]



wherein R<sup>1</sup> and R<sup>2</sup> are the same or different from each other and each represents a hydrogen atom, an alkyl group or a cycloalkyl group; R<sup>3</sup> represents a hydrogen atom or a methyl group; R<sup>4</sup> represents halogen atom, an alkyl group, an oxygen-containing group, amino group or an N-substituted amino group; the Z ring represents a monocyclic or polycyclic alicyclic hydrocarbon ring; in formula (1), R<sup>1</sup> and R<sup>2</sup> may, jointly and together with the adjacent carbon atom, form an alicyclic hydrocarbon ring.

[Claim 2] The acid-responsive compound according to Claim 1 wherein, in the formula (1), R<sup>1</sup> is a hydrogen atom and R<sup>2</sup> is a hydrogen atom or a straight-chain or branched-chain C<sub>1-4</sub> alkyl group.

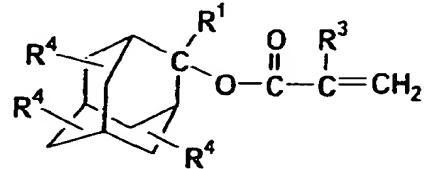
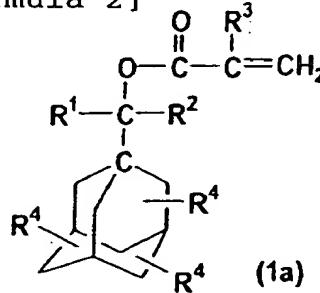
[Claim 3] The acid-responsive compound according to Claim 1 wherein the Z ring is a bridged ring-type hydrocarbon ring comprising 2 to 4 rings.

[Claim 4] The acid-responsive compound according to Claim 1 wherein the oxygen-containing group is at least one substituent selected from the group consisting of oxo group, hydroxyl group, an alkoxy group, carboxyl group, an alkoxy carbonyl group, a cycloalkyloxycarbonyl group, an aryloxycarbonyl group, an aralkyloxycarbonyl group, hydroxymethyl group, carbamoyl group, an N-substituted carbamoyl group and nitro group.

[Claim 5] The acid-responsive compound according to Claim 1 wherein R<sup>4</sup> is a hydroxyl group, an alkoxy group, a carboxyl group, an alkoxy carbonyl group or a hydroxymethyl group.

[Claim 6] The acid-responsive compound according to Claim 1, which is represented by the following formula (1a) or (2a):

[Formula 2]

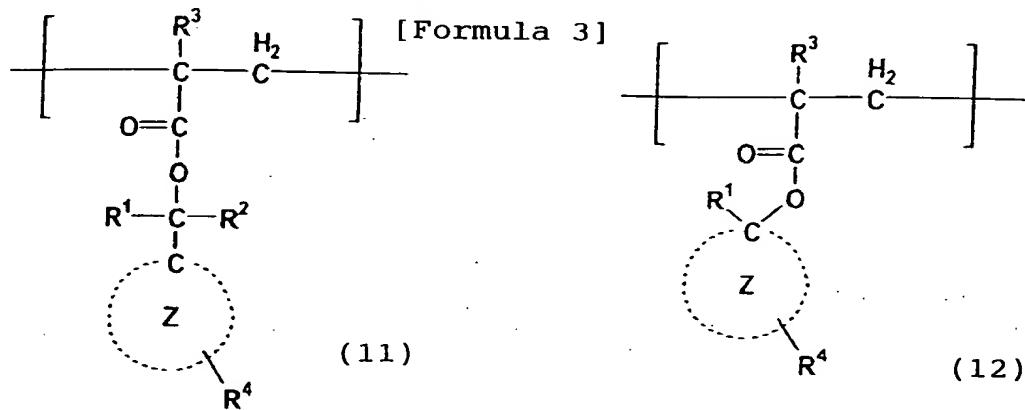


(2a)

wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are as defined above; R<sup>4</sup>'s may be the same or different from each other and each represents hydrogen atom, a halogen atom, an alkyl group, an oxygen-containing group, amino group or an N-substituted amino group with proviso that all R<sup>4</sup>'s are not concurrently hydrogen atoms.

[Claim 7] The acid-responsive compound according to Claim 6 wherein R<sup>1</sup> is a hydrogen atom or a straight-chain or branched-chain C<sub>1-4</sub> alkyl group; R<sup>2</sup> is a hydrogen atom or a straight-chain or branched-chain C<sub>1-4</sub> alkyl group; R<sup>3</sup> is a hydrogen atom or a methyl group; at least one of R<sup>4</sup>'s is at least one oxygen-containing group selected from the group consisting of oxo group, hydroxyl group, an alkoxy group, carboxyl group, an alkoxy carbonyl group, a cycloalkyloxycarbonyl group, an aryloxycarbonyl group, an aralkyloxycarbonyl group, hydroxymethyl group, carbamoyl group, an N-substituted carbamoyl group and nitro group.

[Claim 8] A photoresist resin composition comprising a polymer having at least a unit represented by the following formula (11) or (12):



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and ring  $Z$  are as defined in

and a photoactive acid precursor.

[Claim 9] The photoresist resin composition according to Claim 8 wherein the polymer is a copolymer.

## [Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to acid-responsive compounds including adamantane derivatives and to photoresist resin compositions prepared using the acid-responsive compounds. More particularly, the present invention relates to a photoresist resin composition suitable for the formation of a pattern (e.g. minute (fine) processing of semiconductor) using ultraviolet rays or far-ultraviolet rays (inclusive of excimer laser beams) and an acid-responsive compound therefor.

[0002]

[Background Art]

The semiconductor integrated circuit is fabricated by a lithographic process which comprises forming a resist thin-layer on a substrate, then forming a latent image pattern by imagewise exposure to light, developing the latent image to form a resist pattern, dry-etching the substrate using the resist pattern as a mask, and removing the resist to provide a designed pattern.

[0003]

As the resist for semiconductor manufacture, a photosensitive resin composition containing an alkali-soluble novolac resin and a diazonaphthoquinone derivative is known. This resin composition has been used as a positive-acting resist by taking advantage of the

phenomenon that on exposure to light the diazonaphthoquinone group is decomposed to give a carboxyl group, whereby the composition which is initially alkali-insoluble is rendered alkali-soluble. There also is known a negative-acting resist, that is a resist which becomes insoluble on exposure to light through a photo-crosslinking reaction in the presence of an azide compound or a photopolymerization reaction in the presence of a photopolymerization initiator.

[0004]

Meanwhile, in the lithographic technology, the demand for a finer line pattern definition has caused a shift from ultraviolet rays, such as g-line and i-line, to rays of shorter wavelengths, such as far-ultraviolet rays, vacuum ultraviolet rays, excimer laser beams, an electron beam and X-rays.

[0005]

However, because the resins used contain an aromatic ring, those resists may at times be opaque to light at wavelengths shorter than 200 nm and are not suited (inactive) as compositions for use with an ArF excimer laser which has a wavelength of 193 nm.

[0006]

As a photoresist suitable for short-wavelength exposure light sources (e.g. ArF excimer laser), Japanese Patent Application Laid-Open No. 73173/1997 discloses a resist material comprising a polymer having a structural

unit protected by an alicyclic hydrocarbon group, such as adamantane or norbornane, which is cleaved (eliminated) by an acid to render the material alkali-soluble in combination with an acid precursor. This literature mentions, as the polymer, (1) a copolymer of 2-methyl-2-adamantyl (meth)acrylate and (2) a copolymer of 2-(1-adamantyl)propyl (meth)acrylate, among others. The above polymer having no double bond within its ring structure is transparent (active) to the ArF excimer laser beam and, in semiconductor fine processing, the resistance to plasma gas dry-etching is enhanced.

[0007]

However, when the above resist comprising the polymer and the acid precursor is used to form a pattern, the tendency toward formation of cracks and peeling of the pattern is increased as the pattern line becomes finer so that it is sometimes impossible to form a pattern of fine line definition.

[0008]

[Problems to be Solved by the Invention]

The present invention, therefore, has for its object to provide an acid-responsive compound having an alicyclic hydrocarbon group (e.g. an adamantane skeleton) and capable of providing an alkali-soluble polymer on exposure to light, thus being useful for the formation of fine-line patterns and a photoresist resin composition containing the compound.

[0009]

It is another object of the present invention to provide an acid-responsive compound which is high in sensitivity and etching resistance (particularly resistance to dry etching) and instrumental in forming a fine-line resist pattern with good reproducibility and high precision and a photoresist resin composition containing the compound.

[0010]

It is a still another object of the present invention to provide an acid-responsive compound showing high adhesion to a substrate and useful for forming a fine-line resist pattern with high precision and high reproducibility and a photoresist resin composition containing the compound.

[0011]

[Means to Solve the Problems]

The inventors of the present invention did intensive investigations for accomplishing the above objects and found that when a polymer comprising an acid-responsive compound unit having an alicyclic hydrocarbon group and a specific structure is used in combination with a photoactive acid precursor, the alicyclic hydrocarbon group is stably and efficiently eliminated from the polymer by the acid formed from the acid precursor on exposure to light to thereby enable water or alkali development. The present invention has been developed on the basis of the

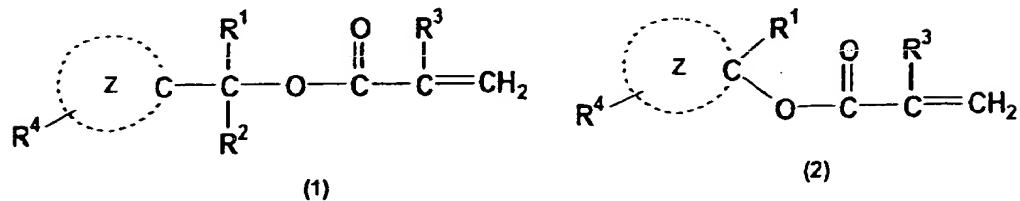
above finding.

[0012]

The acid-responsive compound according to the present invention, therefore, is represented by the following formula (1) or (2).

[0013]

[Formula 4]



[0014]

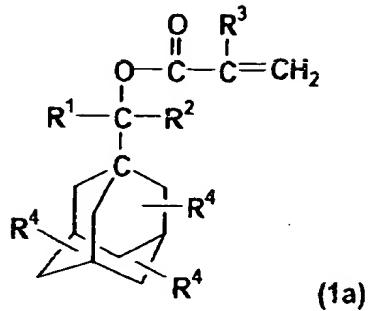
wherein R<sup>1</sup> and R<sup>2</sup> are the same or different from each other and each represents hydrogen atom, an alkyl group or a cycloalkyl group; R<sup>3</sup> represents hydrogen atom or methyl group; R<sup>4</sup> represents a halogen atom, an alkyl group, an oxygen-containing group, amino group or an N-substituted amino group; the Z ring represents a monocyclic or polycyclic alicyclic hydrocarbon ring; in formula (1), R<sup>1</sup> and R<sup>2</sup> may, jointly and together with the adjacent carbon atom, form an alicyclic hydrocarbon ring.

[0015]

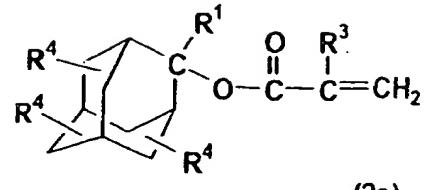
In this acid-responsive compound, the ring Z may be a bridged (clossliked) ring-type hydrocarbon ring containing 2 to 4 component rings (e.g. an adamantine ring). Such compounds include adamantine derivatives represented by the following formula (1a) or formula (2a).

[0016]

[Formula 5]



(1a)



(2a)

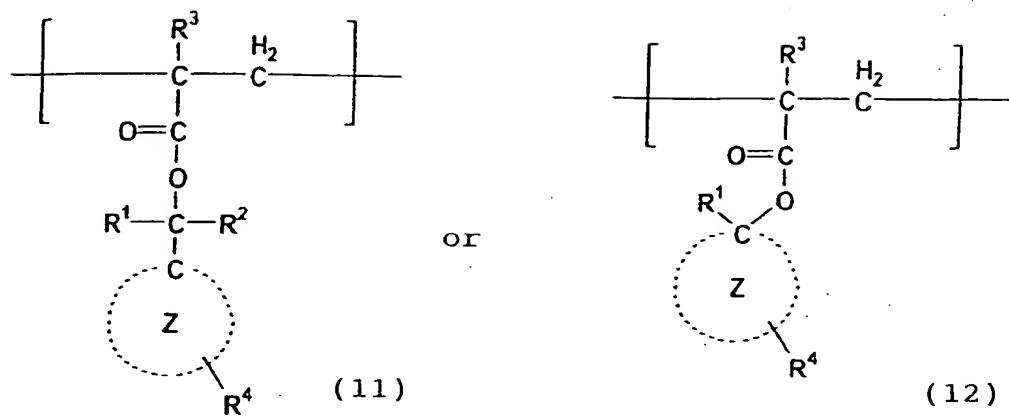
[0017]

wherein R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are as defined above; R<sup>4</sup>'s may be the same or different from each other and each represents hydrogen atom, a halogen atom, an alkyl group, an oxygen-containing group, amino group or an N-substituted amino group with proviso that that all R<sup>4</sup>'s are not hydrogen atoms.

The photoresist resin composition of the present invention can be constituted by a polymer having at least a unit of the following formula (11) or formula (12) and a photoactive acid precursor (a photoactive acid generator).

[0018]

[Formula 6]



wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$ , and Z ring are as defined in

Claim 1.

[0019]

### [Preferred Embodiments of the Invention]

Referring to the above formulas (1), (2), (1a), (2a), (11) and (12), the alkyl groups represented by  $R^1$  and  $R^2$  each includes straight-chain or branched-chain alkyl groups, e.g.  $C_{1-10}$  alkyl groups (preferably  $C_{1-6}$  alkyl groups and particularly  $C_{1-4}$  alkyl groups), such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, s-butyl, and t-butyl, etc.

[ 0020 ]

The branched-chain alkyl group may be an alkyl group containing a tertiary carbon atom. The branched-chain alkyl group having a tertiary carbon atom includes 1-C<sub>1-4</sub> alkyl-C<sub>1-6</sub> alkyl groups such as isopropyl, isobutyl, 1-methylethyl, isopentyl, 1-methylpropyl(s-butyl), 1-methylbutyl(s-pentyl), s-hexyl, 1-ethylethyl, 1-ethylbutyl, etc. The preferred branched-chain alkyl group R<sup>1</sup> includes alkyl groups having a methine carbon atom in

the  $\alpha$ -position, particularly 1- $C_{1-2}$  alkyl- $C_{1-4}$  alkyl(isopropyl, s-butyl, etc.) groups. Referring, further, to formulas (1), (2), (1a), (2a), (11) and (12), when the Z ring has no substituent, the alkyl group designated by  $R^1$  is a branched-chain alkyl group containing a tertiary carbon atom.

[0021]

The cycloalkyl group includes  $C_{3-15}$  cycloalkyl groups, for example monocyclic  $C_{3-10}$  cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclohexyl, cyclooctyl, and cyclodecyl, and polycyclic  $C_{6-15}$  cycloalkyl groups such as perhydronaphthyl (decalyl), adamantyl, methyladamantyl, and dimethyladamantyl.

[0022]

$R^3$  represents hydrogen atom or methyl group, forming an acryloyl or methacryloyl group.

[0023]

$R^1$  and  $R^2$  may, jointly and together with the adjacent carbon atom, form an alicyclic hydrocarbon ring. This alicyclic hydrocarbon ring includes hydrocarbon rings corresponding to the cycloalkyl group.

[0024]

The Z ring includes a variety of alicyclic hydrocarbon rings, for example monocyclic hydrocarbon rings and polycyclic hydrocarbon rings (spiro hydrocarbon ring, ring assembly hydrocarbon ring, fused-ring (condensed ring-type) hydrocarbon ring, and bridged-ring

(crosslinked ring-type) hydrocarbon ring). The monocyclic hydrocarbon ring includes but is not limited to C<sub>4-10</sub> cycloalkane rings such as cycloheptane, cyclohexane, cyclopentane, cyclooctane, etc. and the spiro hydrocarbon ring includes but is not limited to C<sub>8-16</sub> hydrocarbon rings such as spiro[4.4]nonane, spiro[4.5]decane, spirobicyclohexane, etc. The ring assembly hydrocarbon ring includes but is not limited to hydrocarbon rings having C<sub>5-12</sub> cycloalkane rings, such as bicyclohexane ring, biperhydronaphthalene ring, etc. The fused-ring (fused ring-type) hydrocarbon ring includes, for example, fused-ring rings containing 5 to 8-membered cycloalkane component rings such as perhydronaphthalene ring (decalin ring), perhydroanthracene ring, perhydrophenanthrene ring, perhydroacenaphthene ring, perhydrofluorene ring, perhydroindene ring, perhydrophenalene ring, etc.

[0025]

The preferred Z ring is a bridged-ring hydrocarbon ring. The bridged-ring hydrocarbon ring includes but is not limited to bicyclic hydrocarbon rings such as pinane, bornane, norpinane, norbornane, etc.; tricyclic hydrocarbon rings such as homobrendane, adamantane, tricyclo[5.2.1.0<sup>2,6</sup>]decane, tricyclo[4.3.1.1<sup>2,5</sup>]undecane, etc.; tetracyclic hydrocarbon rings such as tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodecane, perhydro-1,4-methano-5,8-methanonaphthalene, etc.; hydrogenated

dimers of dienes [e.g. hydrogenated dimers of cycloalkadienes such as cyclopentadiene, cyclohexadiene, cycloheptadiene, etc. (e.g. perhydro-4,7-methanoindene etc.), butadiene dimer (vinylcyclohexene) and its hydrogenation product, and butadiene-cyclopentadiene dimer (vinylnorbornene) and its hydrogenation product]. The preferred bridged-ring hydrocarbon ring usually has a bornane, norbornane or adamantane skeleton.

The preferred Z ring is a bridged-ring hydrocarbon ring containing 2 to 4 component rings.

[0026]

The Z rings (monocyclic or polycyclic hydrocarbon rings) usually have a substituent  $R^4$ . The Z ring may have a plurality of substituents  $R^4$  and, in such cases, it is only necessary that at least one of  $R^4$ 's is any of the functional groups mentioned below, with the other  $R^4$  or  $R^4$ 's may each represent a hydrogen atom. The substituent  $R^4$  is a halogen atom (e.g. bromine, chlorine or fluorine), an alkyl group (e.g.  $C_{1-4}$  alkyl groups such as methyl, ethyl, butyl, t-butyl, etc.), an oxygen-containing group, an amino group or an N-substituted amino group. The oxygen-containing group includes but is not limited to oxo group, hydroxy group, alkoxy groups (e.g.  $C_{1-4}$  alkoxy groups such as methoxy, ethoxy, t-butoxy, etc.), carboxyl group, alkoxy carbonyl groups (e.g.  $C_{1-4}$  alkoxy carbonyl groups such as methoxycarbonyl, ethoxycarbonyl, butoxycarbonyl, t-butoxycarbonyl, etc.), cycloalkyloxycarbonyl groups (e.g.  $C_{3-10}$  cycloalkyloxycarbonyl groups such as

cyclopropyloxycarbonyl, cyclobutyloxycarbonyl, cyclopentyloxycarbonyl, cyclohexyloxycarbonyl, cycloheptyloxycarbonyl, cyclooctyloxycarbonyl, etc.), aryloxycarbonyl groups (e.g. phenoxy carbonyl), aralkyloxycarbonyl groups (e.g. benzyloxycarbonyl, phenethyloxycarbonyl, trityloxycarbonyl, etc.), hydroxymethyl group, carbamoyl group, N-substituted carbamoyl groups (e.g. N-C<sub>1-4</sub> alkylcarbamoyl groups), and nitro group.

[0027]

The preferred substituent R<sup>4</sup> includes hydroxyl group, alkoxy groups, carboxyl group, alkoxy carbonyl groups and hydroxymethyl group. Particularly, it is preferred that the substituent R<sup>4</sup> is a hydroxyl group, carboxyl group, or hydroxymethyl group.

[0028]

Those substituent groups R<sup>4</sup> each may be protected with a protective group, and this protective group may be a protective group which can be eliminated with an acid, that is to say a protective group which functions as a dissolution-inhibitory modifying group for preventing dissolution of the polymer prior to exposure to light.

[0029]

The protective group for hydroxyl group and hydroxymethyl group includes but is not limited to alkoxy carbonyl groups (C<sub>1-4</sub> alkoxy carbonyl groups such as methoxycarbonyl, ethoxycarbonyl, t-butoxycarbonyl, etc.)

and benzyloxy group.

[0030]

The protective group for carboxyl group includes but is not limited to alkoxy groups ( $C_{1-4}$  alkoxy groups such as methoxy, ethoxy, t-butoxy, etc.), aralkyloxy groups (benzyloxy, p-methoxybenzyloxy, diphenylmethyloxy, benzhydryloxy, etc.) and N-hydroxysuccinimido group.

[0031]

When the substituent  $R^4$  is an oxygen-containing group, it contributes to an improved adhesion between the resist and the substrate.

[0032]

In the above-mentioned compounds, the preferred substituents and combinations thereof are as follows.

(i) In at least one of the component rings forming the  $Z$  ring, the substituent  $R^4$  is an oxygen-containing group, for example at least one member selected from hydroxyl group, alkoxy groups, carboxyl group, alkoxycarbonyl groups and hydroxymethyl group.

[0033]

(ii) In the formula (1),  $R^1$  is a hydrogen atom or a straight-chain or branched-chain  $C_{1-4}$  alkyl group (especially a hydrogen atom) and  $R^2$  is a hydrogen atom or a straight-chain or branched-chain  $C_{1-4}$  alkyl group.

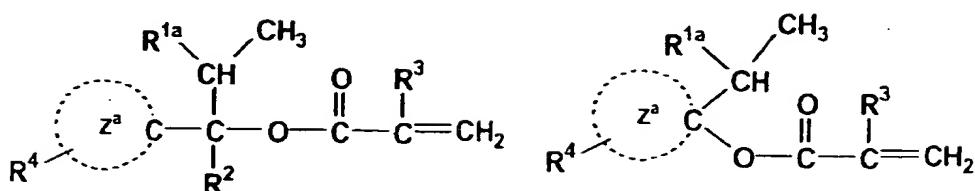
(iii) In the formulas (1), (2), (1a), (2a), (11) and (12),  $R^1$  is a 1-methyl- $C_{1-4}$  alkyl group.

Such acid-responsive compounds include

(meth)acrylic esters of the following formulas.

[0034]

[Formula 7]



[0035]

wherein  $R^{1a}$  represents a  $C_{1-3}$  alkyl group;  $R^3$  represents a hydrogen atom or a methyl group; and the  $Z^a$  ring represents a bridged alicyclic hydrocarbon ring having the substituent  $R^4$ .

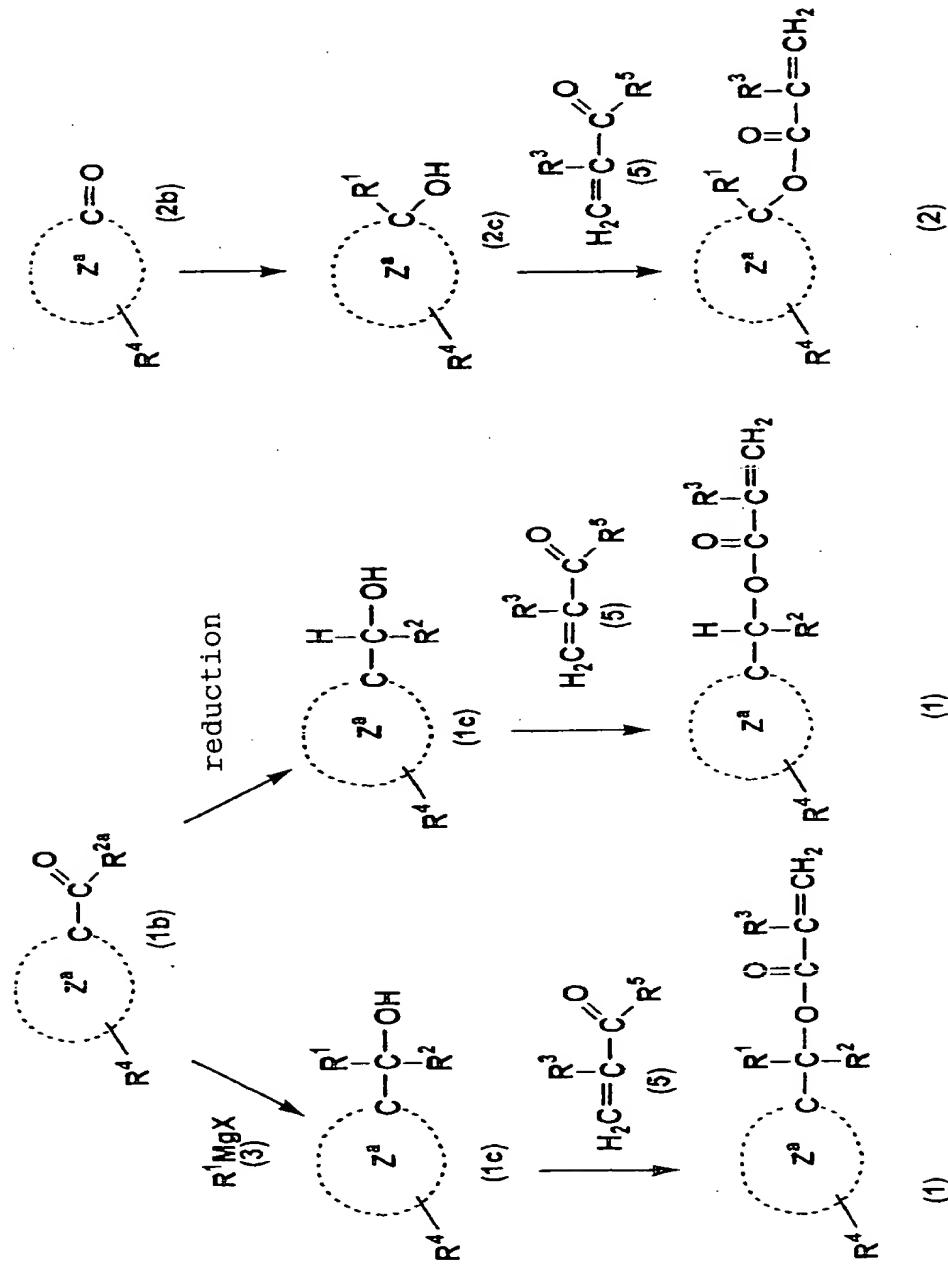
When, in the formulas (1), (2), (1a), (2a), (11) and (12), the Z ring has no substituent,  $R^1$  is a branched-chain alkyl group having a tertiary carbon atom.

[0036]

The acid-responsive compounds (1) and (2) of the present invention can be prepared, for example, in accordance with the following reaction schemes.

[0037]

[Formula 8]



[0038]

wherein  $X$  represents halogen atom;  $R^{2a}$  means the same as  $R^2$  or represents a halogen atom;  $R^5$  represents a halogen atom or hydroxyl group, an alkoxy group, an alkenyloxy group or an alkynyloxy group;  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and the  $Z$  ring are

as defined hereinbefore.

The halogen atom typically includes chlorine, bromine and iodine, and the alkoxy group includes but is not limited to C<sub>1-10</sub> alkoxy groups (e.g. methoxy, ethoxy, t-butoxy, etc.). The alkenyloxy group includes but is not limited to C<sub>2-10</sub> alkenyloxy groups (e.g. vinyloxy, allyloxy, 1-propenyloxy, isopropenyloxy, 1-butenyloxy, 2-butenyloxy, 3-butenyloxy, 2-pentenyloxy, etc.), and the alkynyloxy group includes but is not limited to C<sub>2-10</sub> alkynyloxy groups (e.g. ethynyloxy, propynyloxy, etc.).

[0039]

Referring to the above reaction schemes, the carbonyl compound (1b) includes, to mention typical examples, monocyclic compounds (cycloalkyl-1-C<sub>2-6</sub> alkanones such as cyclohexyl-1-ethanone etc.), spiro compounds (e.g. spiro[4.5]decan-8-yl-1-ethanone, spirobicyclohexan-9-yl-1-ethanone, etc.), ring assembly compounds (e.g. bicycloalkyl-1-C<sub>2-6</sub> alkanones such as bicyclohexan-4-yl-1-ethanone etc.), fused-ring compounds (e.g. perhydronaphthyl-1-ethanone, perhydrophenanthrenyl-1-ethanone, etc.), bridged-ring compounds (e.g. bicyclic compounds such as bornan-2-yl-1-ethanone, bornan-3-yl-1-ethanone, norbornan-2-yl-1-ethanone, etc. and tricyclic compounds such as adamantyl-1-C<sub>2-6</sub> alkanones, e.g. adamantan-1-yl-ethan-1-one, adamantan-1-yl-propan-1-one, adamantan-1-yl-butan-1-one, methyladamantan-1-yl-ethan-1-one, etc.); and derivatives from hydrogenated

dimers of dienes (e.g. perhydro-4,7-methanoindenyl-1-C<sub>2-6</sub> alkanones such as perhydro-4,7-methanoinden-1-yl-1-ethanone etc.).

[0040]

The carbonyl compound (1b) in which R<sup>2a</sup> is a halogen atom, i.e. the acid halide, includes but is not limited to monocyclic compounds (cyclohexanecarbonyl halides etc.), spiro compounds (spiro[4.5]decane-8-carbonyl halides etc.), ring assembly compounds (bicyclohexane-4-carbonyl halides etc.), fused-ring compounds (perhydronaphthalene-1-carbonyl halides, perhydrophenanthrene-1-carbonyl halides etc.), bridged-ring compounds (bicyclic compounds such as bornane-2-carbonyl halides, norbornane-2-carbonyl halides, etc. and tricyclic compounds such as adamantine-1-carbonyl halides etc.), and derivatives from hydrogenated dimers of dienes (perhydro-4,7-methanoindene-1-carbonyl halides etc.).

[0041]

The carbonyl compound (2b) includes but is not limited to monocyclic ketones (e.g. cycloalkanones such as cyclohexanone, methylcyclohexanone, etc.), spiro-ring ketones (spiro[4.5]decan-8-one, spirobicyclo-hexan-9-one, etc.), ring assembly ketones (e.g. bicycloalkanones such as bicyclohexan-4-one etc.), fused-ring compounds (perhydronaphthalen-1-one, perhydronaphthalen-2-one, perhydrophenanthren-1-one, etc.), bridged-ring compounds

(e.g. bicyclic compounds such as bornan-2-one, bornan-3-one, norbornan-2-one and tricyclic compounds such as adamantanone, methyladamantanone, dimethyladamantanone, etc.), and derivatives from hydrogenated dimers of dienes (e.g. perhydro-4,7-methanoinden-1-one etc.).

[0042]

In the above reaction schemes, the reaction of the carbonyl compound (1b) or (2b) with the reagent  $R^1MgX$  (3) can be carried out according to the conventional Grignard reaction. The amount of the Grignard reagent  $R^1MgX$  (3) relative to 1 mol of the carbonyl compound (1b) or (2b) may for example be about 0.8 to 3 mols (e.g. 1 to 2.5 mols), preferably about 1 to 2 mols, more preferably about 1 to 1.5 mols. When the carbonyl compound (1b) to be used has a halogen atom for  $R^{2a}$ , the compound (1c) wherein  $R^2$  is the same as  $R^1$  can be produced by reacting 2 mols of the Grignard reagent  $R^1MgX$  (3) relative to 1 mol of the carbonyl compound (1b).

[0043]

This reaction can be conducted in an inert solvent to the reaction, such as hydrocarbons (hexane, cyclohexane, etc.), ethers (dimethyl ether, diethyl ether, tetrahydrofuran, etc.), to mention just a few preferred solvents. The reaction temperature can be suitably selected from the range of, for example, about 0 to 100°C, preferably about 10 to 50°C.

[0044]

The reduction reaction of carbonyl compound (1b) (wherein the carbonyl compound corresponding to  $R^{2a}=R^2$ ) with a reducing agent can be carried out according to a conventional method, for example by catalytic hydrogenation using hydrogen as the reducing agent or by the reduction reaction using a hydrogenation reducing agent.

[0045]

The catalyst for the catalytic hydrogenation includes but is not limited to elemental metals (simple metals) such as platinum, palladium, nickel, cobalt, iron and copper and compounds containing such metal elements (e.g. platinum oxide, palladium black, palladium-carbon, copper chromite, etc.). The amount of the catalyst is generally about 0.02 to 1 mol relative to 1 mol of the substrate. The reaction temperature for catalytic hydrogenation may for example be about -20°C to 10°C (e.g. 0 to 70°C). The hydrogen pressure is generally 1 to 10 atmospheres in many instances.

[0046]

Referring to the reduction reaction using a hydrogenation reducing agent, the hydrogenation reducing agent which can be used includes but is not limited to aluminum hydride, lithium aluminum hydride, sodium boron hydride, lithium boron hydride and diborane. The amount of the hydrogenation reducing agent used relative to 1 mol of the substrate is generally not less than 1 mol (for

example, about 1 to 10 mols) in many instances. In many cases of reduction using a hydrogenation reducing agent, the reaction temperature is generally about 0 to 200°C (for example 0 to 170°C).

[0047]

The above reduction reaction (catalytic hydrogenation method, the process using a hydrogenation reducing agent) may be carried out in a solvent inert to the reduction reaction (for example, hydrocarbons, carboxylic acids, ethers, esters and amides).

[0048]

The hydroxy compound (1c) or (2c) formed by the reaction, optionally isolated, is subjected to the esterification reaction using (meth)acrylic acid or a derivative thereof (5) to give the acid-responsive compound (1) or (2).

[0049]

The (meth)acrylic acid or its derivative (5), mentioned above, includes (meth)acrylic acid, (meth)acrylic anhydride, and reactive derivatives having a leaving group [e.g. acid halides ((meth)acryloyl chloride, (meth)acryloyl bromide, etc.), (meth)acrylic acid alkyl esters such as C<sub>1-6</sub> alkyl (meth)acrylates (e.g. methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, etc.), (meth)acrylic acid alkenyl esters (e.g. C<sub>2-10</sub> alkenyl

(meth)acrylates such as vinyl (meth)acrylate, allyl (meth)acrylate, 1-propenyl (meth)acrylate, isopropenyl (meth)acrylate, 1-butenyl (meth)acrylate, 2-butenyl (meth)acrylate, 3-butenyl (meth)acrylate, 2-pentenyl (meth)acrylate, etc.), and alkynyl esters of (meth)acrylic acid (e.g. C<sub>2-10</sub> alkynyl (meth)acrylates such as ethynyl (meth)acrylate, propynyl (meth)acrylate, etc.]).

[0050]

The preferred compound (5) includes (meth)acrylic acid, (meth)acryloyl halides, C<sub>1-6</sub> lower alkyl esters of (meth)acrylic acid, C<sub>2-6</sub> alkenyl esters of (meth)acrylic acid, and C<sub>2-6</sub> alkynyl esters of (meth)acrylic acid. Particularly with a (meth)acryloyl halide or a C<sub>2-6</sub> alkenyl (meth)acrylate, the corresponding acid-responsive compound can be obtained with high selectivity and in high yield through a leaving group exchange reaction while side reactions such as addition polymerization are inhibited.

[0051]

The above esterification reaction can be carried out by a conventional manner, for example in the presence of a suitable catalyst (an acid catalyst). When a (meth)acryloyl halide is used, there are cases in which the acid-responsive compound is contaminated with the halogen component. Therefore, this esterification reaction is preferably effected by the esterification reaction using (meth)acrylic acid or the transesterification reaction. The esterification

reaction and transesterification reaction can be conducted using the conventional esterification catalyst (for example a non-halogen series inorganic acid such as sulfuric acid, hydrochloric acid, a sulfonic acid such as p-toluenesulfonic acid, a protonic acid such as acidic ion exchange resin, a Lewis acid such as boron trifluoride, an enzyme, etc.) and a transesterification catalyst (for example, the esterification catalysts, alkali metal alkoxide such as sodium alkoxides, aluminum alkoxides, titanic acid esters, etc.).

[0052]

To enhance the reaction efficiency and obtain the objective acid-responsive compound in high yield, the esterification reaction (inclusive of leaving group exchange reactions such as transesterification) between the hydroxy compound (1c) or (2c) and (meth)acrylic acid or a derivative thereof (5) is conducted with advantage in the presence of a catalyst comprised of a compound of a Group 3 element of Periodic Table of the Elements. In the reaction utilizing such a catalyst, the formation of the amine hydrochloride can be inhibited and, when a C<sub>1-4</sub> lower alkyl ester or C<sub>2-4</sub> alkenyl ester of (meth)acrylic acid is used, the objective compound can be protected against contamination with the halogen component. Moreover, because a low-boiling compound (e.g. the above ester) can be used as the (meth)acrylic acid or derivative (5), the treatment after the reaction is easy and the

isolation yield can be dramatically increased.

[0053]

Referring to the catalyst comprised of a compound of Group 3 element, the Group 3 element includes rare earth elements, e.g. scandium, yttrium, lanthanide series elements (lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium)], and actinoid series elements (e.g. actinium etc.). The preferred Group 3 element includes rare earth elements, such as scandium, yttrium, and lanthanoid series elements (samarium, gadolinium, ytterbium, etc.).

[0054]

The valence of the Group 3 element is not particularly restricted but is often bivalent to tetravalent, particularly bivalent or trivalent. The compound of Group 3 element, mentioned above, is not particularly restricted only if it has the necessary catalyst activity, and may be an elemental metal or a compound or complex of the metal with an inorganic compound (e.g. a halide, oxide, double oxide, phosphorus compound or nitrogen compound) or an organic compound (e.g. an organic acid). In many instances, it is the hydroxide or oxo-acid salt, organic acid salt, inorganic acid salt or halide containing the metal element or a coordination compound (complex) containing the metal element. The complex may be a  $\pi$  complex such as a metallocene compound. Furthermore, the compound of Group

3 element may be a double salt compound (complex metal compound) with another metal. Those catalysts can be used each alone or in a combination of two or more species.

[0055]

The catalyst component is now described in further detail taking a samarium compound as an example, it being, however, to be understood that the compounds of other Group 3 elements which correspond to the samarium compound can be used likewise with success.

[0056]

The hydroxide includes samarium (II) hydroxide and samarium (III) hydroxide, for instance, and the metal oxide includes samarium (II) oxide and samarium (III) oxide, for instance.

[0057]

The organic acid salt includes but is not limited to salts with such organic acids as organic carboxylic acids (monocarboxylic acids, polycarboxylic acids), hydroxycarboxylic acids, thiocyanic acid or sulfonic acids (alkylsufonic acids, benzenesufonic acid, arylsulfonic acids, etc.). The inorganic acid salt includes but is not limited to the nitrate, sulfate, phosphate, carbonate and perchlorate. The organic acid salt and inorganic acid salt, mentioned above, include but are not limited to samarium acetate, samarium trichloroacetate, samarium trifluoroacetate, samarium trifluoromethanesulfonate (i.e. samarium triflate), samarium nitrate, samarium

sulfate, samarium phosphate and samarium carbonate.

[0058]

The halide may for example be the fluoride, chloride, bromide or iodide.

[0059]

The ligand forming the complex includes OH (hydroxo), alkoxy, acyl, alkoxy carbonyl, acetyl acetonato, cyclopentadienyl,  $C_{1-4}$  alkyl-substituted cyclopentadienyl (e.g.  $C_{1-2}$  alkyl-substituted cyclopentadienyl groups such as pentamethylcyclopentadienyl etc.), dicyclopentadienyl,  $C_{1-4}$  alkyl-substituted dicyclopentadienyl (e.g.  $C_{1-2}$  alkyl-substituted dicyclopentadienyl such as pentamethyldicyclopentadienyl etc.), halogen, CO, CN, oxygen,  $H_2O$  (aqua), phosphorus compounds such as phosphines, nitrogen-containing compounds such as  $NH_3$  (ammine), NO,  $NO_2$  (nitro),  $NO_3$  (nitrato), ethylenediamine, diethylenetriamine, pyridine, phenanthroline, etc.

Referring to the complexes or complex salts, one or more similar or dissimilar ligands may be coordinated.

[0060]

Among the complexes, samarocene complexes include diacetyl acetonato samarium (II), triacetyl acetonato samarium (III), dicyclopentadienyl samarium (II), tricyclopentadienyl samarium (III), dipentamethyl-cyclopentadienyl samarium (II) and tripentamethylcyclopentadienyl samarium (III).

[0061]

When the compound of Group 3 element [the bivalent samarocene complex having the pentamethylcyclopentadienyl ligands which are highly electron-donative  $[(C_5Me_5)_2Sm; (PMSm)]$  or any of samarium compounds such as samarium halides, alkoxide, hydroxide, etc.] is used as the catalyst, esterification proceeds with a higher efficiency and with side reactions inhibited as compared with the reaction in the presence of a Lewis acid catalyst or a protonic acid catalyst even in esterification reactions which are handicapped as equilibrium reactions. Thus, this catalyst is useful for producing the acid-responsive compounds (1) and (2) by a leaving group exchange reaction such as transesterification.

[0062]

The catalyst comprised of a compound of Group 3 element may be a homogeneous system or a heterogeneous system. Moreover, the catalyst may be an solid catalyst comprising the compound of Group 3 element supported on a support or carrier. The support is usually a porous support such as activated carbon, zeolite, silica, silica-alumina, bentonite or the like. The amount of the supported catalyst component is about 0.1 to 50 parts by weight, preferably about 0.5 to 30 parts by weight, more preferably about 1 to 20 parts by weight relative to 100 parts by weight of the support.

[0063]

The amount of the catalyst (e.g. the catalyst comprised of the compound of Group 3 element) can be liberally selected from a broad range, for example the range of about 0.1 mol % to 1 equivalent, preferably about 0.5 to 50 mol %, more preferably about 1 to 25 mol % (e.g. about 5 to 20 mol %), based on the hydroxy compound (1c) or (2c).

[0064]

The esterification reaction mentioned above (particularly the reaction using the compound of Group 3 element as the catalyst) may be conducted in the presence of an oxime. The oxime may be whichever of an aldoxime or a ketoxime and includes aliphatic oximes such as 2-hexanone oxime etc., alicyclic oximes such as cyclohexanone oxime etc., and aromatic oximes such as acetophenone oxime, benzophenone oxime, benzyl dioxime, etc.

[0065]

The amount of the oxime can be selected from a broad range, for example the range of about 0.1 mol % to 1 equivalent, preferably about 1 to 50 mol %, more preferably about 5 to 40 mol % (e.g. about 5 to 30 mol %), based on the hydroxy compound (1c) or (2c).

[0066]

The ratio of (meth)acrylic acid or its derivative (5) to hydroxy compound (1c) or (2c) is about 0.5 to 5 mols, preferably about 0.8 to 5 mols, more preferably not less than 1 mol (e.g. about 1 to 3 mols, particularly about 1 to 1.5 mols) of (meth)acrylic acid or derivative (5) per

equivalent of hydroxy compound (1c) or (2c) (that is the weight of the hydroxy compound per hydroxyl group). Since the esterification reaction is an equilibrium-controlled reaction, it is more advantageous to use a larger proportion of (meth)acrylic acid or derivative thereof (5) for accelerating the reaction but because of the usually high catalyst activity of the compound of Group 3 element, (meth)acrylic acid or derivative thereof (5) need not be used in a large excess. Particularly, in the reaction involving a combination of reactants which is very unfavorable from the standpoint of reaction equilibrium, the use of the alkenyl ester having a vinyl leaving group (e.g. vinyl ester) as the (meth)acrylic acid or derivative thereof (5) rather leads, in many instances, to an early completion of reaction and a better result even if the compound (1c) is used in a proportion of only 1 mol or less (e.g. 0.4 to 1 mol, particularly 0.5 to 1 mol) per equivalent of the leaving group of hydroxy compound (1c) or (2c).

[0067]

In the process using the catalyst, the heat of reaction is not so high as in the process using an acid halide such as (meth)acryloyl chloride so that the reaction can be smoothly conducted in a small amount of solvent and the end product can be obtained in a higher yield.

[0068]

The esterification reaction mentioned above can be carried out in the presence or absence of a solvent inert

to the reaction. The reaction solvent which can be used includes but is not limited to aliphatic hydrocarbons, alicyclic hydrocarbons, aromatic hydrocarbons, polar aprotic solvents such as ketones, ethers, amides, N-methylpyrrolidone, nitriles, etc. and mixed solvents thereof. As the reaction solvent, (meth)acrylic acid or derivative thereof (5) may be used.

[0069]

When a highly hydrophilic species of hydroxy compound (1c) or (2c) is used, the solvent may be a hydrophilic solvent (ketones such as acetone, methyl ethyl ketone, etc., ethers such as dioxane, diethyl ether, tetrahydrofuran, etc., and other polar aprotic solvents), or a mixed solvent of a hydrophilic solvent and a hydrophobic solvent (an aliphatic, alicyclic or aromatic hydrocarbon).

[0070]

Since the above reaction is an equilibrium-controlled reaction, it is advantageous to remove the reaction-interfering components such as the cleaved (eliminated) component from the reaction system for accelerating the reaction. For removal of the eliminated component, it is advantageous to use a high-boiling solvent (for example an organic solvent boiling at 50 to 120°C, particularly about 60 to 115°C) or an azeotropic solvent (for example the hydrocarbons).

[0071]

The esterification reaction temperature can be

selected from the range of, for example, about 0 to 150°C, preferably about 25 to 120°C. When the catalyst comprised of the compound of Group 3 element is used, the acid-responsive compound forms with high efficiency even under mild conditions. Thus, the reaction temperature may for example be about 0 to 150°C, preferably about 10 to 100°C, more preferably about 20 to 80°C. Particularly when the alkenyl ester, for instance, is used as the (meth)acrylic acid or derivative (5), the reaction can be smoothly carried through even under mild conditions, namely at about 20 to 50°C. The reaction can be conducted at atmospheric pressure, under applied pressure or at elevated pressure. Moreover, the reaction can be carried out batchwise, semi-batchwise or continuously in the conventional manner.

[0072]

After completion of the reaction, the acid-responsive compound (1) or (2) can be easily isolated and purified by such separatory means as filtration, concentration, distillation, extraction, crystallization, recrystallization, column chromatography, etc. as applied independently or in combination.

[0073]

[Photoresist resin composition]

The photoresist resin composition of this invention is characterized in that at least a polymer containing the unit of formula (11) or (12) (e.g. a unit having an adamantine skeleton) and a photoactive acid precursor

(photoactive acid generator) are used in combination and that the polymer is solubilized by irradiation with light. Thus, probably because the ester bond (linkage) which is adjacent to the bulky, hydrophobic Z ring is stably eliminated with high efficiency by the acid produced by the irradiation, a fine-line resist pattern can be formed with high accuracy and reproducibility while the high sensitivity and high etching resistance are maintained.

[0074]

Furthermore, because a polymer containing the acid-responsive compound (1) or (2) as a repeating unit is highly soluble in a organic solvent for photoresist use, the precipitation of the polymer can be prevented and the stability of the photoresist solution be improved. In addition, because of the high adhesion of the solution to the substrate, resist patterns can be obtained with high accuracy. Moreover, the cleaning and removing by a development procedure such as dry etching after pattern exposure can be neat and thorough so that the sensitivity of pattern formation is high.

[0075]

Particularly when the substituent group R<sup>4</sup> on the Z ring has a hydroxyl, alkoxy, carboxyl, alkoxy carbonyl or hydroxymethyl group or a group derived from any of such groups, marked improvements can be realized in the above-mentioned characteristics. Moreover, when the Z ring is an alicyclic hydrocarbon ring, the dry-etching

resistance is high and particularly when it is a polycyclic hydrocarbon ring, the degree of developer-induced swelling is low so that the circuit pattern can be formed with good accuracy.

[0076]

The polymer mentioned above may be a homopolymer or a copolymer of the acid-responsive compound or compounds represented by formula (1) or/and (2) or a copolymer of the acid-responsive compound or compounds of formula (1) or/and (2) with one or more other copolymerizable monomers.

[0077]

The copolymerizable monomers mentioned above include but are not limited to (meth)acrylic monomers (e.g. (meth)acrylic  $C_{1-10}$  alkyl esters such as methyl (meth)acrylate, ethyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth)acrylate, s-butyl (meth)acrylate, t-butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, etc.; (meth)acrylic hydroxy  $C_{2-6}$  alkyl esters such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, etc.; glycidyl (meth)acrylate, (meth)acrylonitrile, cyclohexyl (meth)acrylate, phenyl (meth)acrylate, etc.), styrenic monomers (styrene,  $\alpha$ -methylstyrene, vinyltoluene, etc.), vinyl ester monomers (vinyl acetate, vinyl propionate, etc.), carboxyl group-containing monomers ((meth)acrylic acid, maleic anhydride, itaconic acid, maleic monoesters,

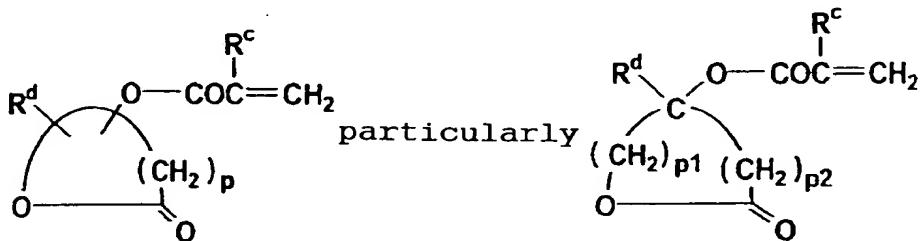
etc.), sulfonic acid group-containing monomers (styrenesulfonic acid etc.), lactone ring-containing monomers, and monomers having an alicyclic hydrocarbon ring.

[0078]

The lactone ring-containing monomers include but are not limited to (meth)acrylic monomers of the following formula:

[0079]

[Formula 9]



[0080]

wherein  $R^c$  represents hydrogen atom or methyl group;  $R^d$  represents hydrogen atom or a  $C_{1-4}$  alkyl group;  $p$  represents an integer of about 2 to 15;  $p_1$  and  $p_2$  each represents an integer of about 0 to 8;  $p_1+p_2$  = about 1 to 14

and the allyl monomers corresponding to the above monomers.

[0081]

The  $C_{1-4}$  alkyl group mentioned for  $R^d$  includes methyl, ethyl, propyl, isopropyl, butyl, isobutyl and t-butyl.  $R^d$  is usually a hydrogen atom or a methyl group. The integer

*p* is usually about 3 to 10, particularly about 3 to 6. Moreover, *p*<sub>1</sub> and *p*<sub>2</sub> each is usually an integer of 0 to 8, and *p*<sub>1</sub>+*p*<sub>2</sub> = about 2 to 9 (preferably 2 to 5). The numbers and substitution positions of the (meth)acryloyloxy group, allyloxy group and *R*<sub>d</sub> are not particularly restricted; thus, they may be located in suitable positions on the lactone ring.

[0082]

The monomer having an alicyclic hydrocarbon ring includes but is not limited to (meth)acrylates having a monocyclic hydrocarbon ring and (meth)acrylates having a polycyclic hydrocarbon ring (spiro hydrocarbon ring, ring assembly hydrocarbon ring, fused-ring hydrocarbon ring and bridged-ring hydrocarbon ring). The (meth)acrylates having a monocyclic hydrocarbon ring include but are not limited to C<sub>4-10</sub> cycloalkyl (meth)acrylates such as cycloheptyl (meth)acrylate, cyclohexyl (meth)acrylate, cyclopentyl (meth)acrylate, and cyclooctyl (meth)acrylate. The (meth)acrylates having a spiro hydrocarbon ring include but are not limited to (meth)acrylates having a spiro C<sub>8-16</sub> hydrocarbon ring, such as spiro[4.4]nonyl (meth)acrylate, spiro[4.5]decanyl (meth)acrylate and spirobicyclohexyl (meth)acrylate. The (meth)acrylates having a ring assembly hydrocarbon ring include but are not limited to (meth)acrylates having C<sub>5-12</sub> cycloalkane rings such as bicyclohexyl (meth)acrylate, and the (meth)acrylates having a fused-ring hydrocarbon ring

include but are not limited to (meth)acrylates having a 5 to 8-membered cycloalkane fused ring, such as perhydronaphthyl (meth)acrylate, perhydroanthryl (meth)acrylate, etc.

[0083]

The (meth)acrylates having a bridged-ring hydrocarbon ring include but are not limited to (meth)acrylates having a bicyclic hydrocarbon ring, such as bornyl (meth)acrylate, norbornyl (meth)acrylate, isobornyl (meth)acrylate, isobornyloxyethyl (meth)acrylate, etc.; (meth)acrylates having a tricyclic hydrocarbon ring, such as dicyclopentadienyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentyloxyalkyl (meth)acrylates, tricyclodecanyl (meth)acrylate, tricyclo[5.2.1.0<sup>2,6</sup>]decanyl (meth)acrylate, tricyclodecanyloxyethyl (meth)acrylate, tricyclo[4.3.1.1<sup>2,5</sup>]undecanyl (meth)acrylate, adamantlyl (meth)acrylate, etc.; and (meth)acrylates having a tetracyclic hydrocarbon ring such as a tetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodecane ring, a perhydro-1,4-methano-5,8-methanonaphthalene ring, etc.

[0084]

Those copolymerizable monomers may have a variety of substituents (e.g. polar groups such as oxo, hydroxyl, alkoxy, carboxyl, alkoxycarbonyl, cycloalkyloxycarbonyl, aryloxycarbonyl, aralkyloxycarbonyl, hydroxymethyl, carbamoyl, N-substituted carbamoyl, nitro, etc.). Those

copolymerizable monomers can be used each alone or in a combination of two or more species.

[0085]

The proportion of the acid-responsive compound (1), (2) in the copolymer may for example be about 10 to 100 weight % (e.g. 15 to 90 weight %), preferably about 25 to 100 weight % (e.g. 30 to 75 weight %), more preferably about 30 to 100 weight % (e.g. 35 to 70 weight %).

[0086]

The photoactive acid precursor which can be used includes the conventional compounds which, when exposed to light, form acids (protic acids or Lewis acids) with high efficiency, for example diazonium salts, iodonium salts, sulfonium salts, oxathiazole derivatives, s-triazine derivatives, imide compounds, oxime sulfonates, diazonaphthoquinone, sulfonic esters [1-phenyl-1-(4-methylphenyl)sulfonyloxy-1-benzoylmethane, 1,2,3-trisulfonyloxymethylbenzene, 1,3-dinitro-2-(4-phenylsulfonyloxymethyl)benzene, 1-phenyl-1-(4-methylphenyl)sulfonyloxymethyl-1-hydroxy-1-benzoylmethane, disulfone derivatives (diphenyl disulfone etc.), benzoin tosylate, etc.] or Lewis acids (triphenylsulfonium hexafluoroantimonate  $((\text{Ph})_3\text{S}^+\text{SbF}_6^-)$ , triphenylsulfonium hexafluorophosphate  $((\text{Ph})_3\text{S}^+\text{PF}_6^-)$ , triphenylsulfonium methanesulfonyl  $((\text{Ph})_3\text{S}^+\text{CH}_3\text{SO}_3^-)$ , diphenyliodonium hexafluorophosphate, etc.). In the above description, Ph represents a phenyl group.

[0087]

Those photoactive acid precursors can be used each alone or in a combination of two or more species.

[0088]

The amount of the photoactive acid precursor can be selected according to the strength of the acid that will be produced by irradiation and the amount of the acid-responsive compound, among other conditions, for example from the range of about 0.1 to 30 parts by weight, preferably about 1 to 25 parts by weight, more preferably about 2 to 20 parts by weight, relative to 100 parts by weight of the polymer.

[0089]

The photoresist resin composition may contain an alkali-soluble component such as alkali-soluble resin (novolac resin, phenolic resin, carboxyl-containing resin, etc.), a coloring agent (dye), an organic solvent, etc. The organic solvent includes but is not limited to hydrocarbons, halogenated hydrocarbons, alcohols, esters, ketones, ethers, cellosolves (methylcellosolve, ethylcellosolve, butylcellosolve, etc.), carbitols, glycol ether esters (mono- or polyalkylene glycol monoalkyl ether esters, cellosolve acetates such as ethylcellosolve acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, etc.) and mixed solvents thereof. The polymer containing the acid-responsive compound (the compound in which the

$Z$  ring has the substituent  $R^4$ ) as a constituent unit is characteristically well-soluble in the organic solvent component of the photoresist.

[0090]

Further, the photoresist resin composition may be freed of contaminants by the conventional separation and purification procedure such as the use of a filter.

[0091]

The photoresist resin composition of this invention can be prepared by mixing the polymer and the photoactive acid precursor. After this photoresist resin composition is coated on a substrate or base and dried, the resulting layer (resist film) is exposed to light through a given mask to form a latent pattern and then developed, providing a fine-line pattern with high accuracy. The sensitivity and the pattern resolution are high.

[0092]

The substrate or base can be selected according to the intended use of the photoresist resin composition and may for example be a silicon wafer or a metal, plastic, glass, ceramic or other substrate. The coating with the photoresist resin composition can be effected by the conventional procedure suited to each application, for example by the spin coating technique or the roll coating technique. The thickness of coating layer comprising the photoresist resin composition can be judiciously selected from the range of, for example, about 0.1 to 20  $\mu\text{m}$ .

[0093]

For the exposure to light, light beams of various wavelengths, e.g. ultraviolet rays and X-rays, can be employed. For the exposure of resists for semiconductor manufacturing, g-line, i-line, and excimer laser (e.g. XeCl, KrF, KrCl, ArF, ArCl, etc.) beams can be utilized.

[0094]

The exposure beam energy can be selected from the range of, for example, about 1 to 1000 mJ/cm<sup>2</sup>, preferably about 10 to 500 mJ/cm<sup>2</sup>.

[0095]

On irradiation, an acid is generated from the acid precursor and the group containing the Z ring (usually the alcohol containing the Z ring) is eliminated by the generated acid and a carboxyl group contributory to solubilization is generated. Therefore, the desired pattern can be formed using an aqueous developer or an alkali developer. Particularly because the photoresist resin composition of the present invention has the Z ring, such as an adamantane skeleton, it is highly resistant to etching (dry etching in particular) so that an elaborate circuit pattern can be formed with high accuracy. Incidentally, the cleavage of the group containing the Z ring may be promoted by exposure and post-exposure baking (PEB).

[0096]

The present invention can be embodied in various

applications, such as circuit-forming materials (resists for semiconductor manufacturing, printed circuit boards, etc.) and image-forming materials (printing plates, relief images, etc.).

[0097]

[Introduction of functional groups]

The acid-responsive compounds (1) and (2) and the polymer component units (11) and (12) have the substituent  $R^4$  as mentioned above. The substituent  $R^4$  can be introduced in a suitable stage among the above-described reaction stages or after completion of the relevant reaction. The hydroxyl group, for instance, can be given by a conventional oxidation process using nitric acid or chromic acid, an oxidation process using oxygen with a cobalt salt as the catalyst or a biochemical oxidation process, for instance, or generated by a method which comprises introducing a halogen atom (e.g. a bromine atom) and then carrying out a hydrolysis reaction using an inorganic salt such as silver nitrate or silver sulfate to thereby introduce a hydroxyl group. As a preferred method, the method using an oxidation catalyst as described in Japanese Patent Application Laid-Open No.327626/1997, for instance, can be mentioned. In this oxidation method, the substrate compound of formula (1a), (2a), (1b), (2b), (1c) or (2c) or the polymer component unit (11) or (12) can be oxidized with oxygen in the presence of an oxidation catalyst comprised of a certain imide compound or an oxidation

catalyst comprised of the imide compound and a co-catalyst to thereby introduce a hydroxyl group.

[0098]

The imide compound mentioned above includes compounds having N-hydroxyimide groups (e.g. aliphatic, alicyclic and aromatic compounds each having about 1 to 3 N-hydroxyimido groups), such as N-hydroxysuccinimide, N-hydroxymaleimide, N-hydroxyhexahydrophthalimide, N,N'-dihydroxycyclohexanetetracarboximide, N-hydroxyphthalimide, N-hydroxytetrabromophthalimide, N-hydroxytetrachlorophthalimide, N-hydroxyhetimide, N-hydroxyhimimide, N-hydroxytrimellitimide, N,N'-dihydroxypyromellitimide, and N,N'-dihydroxynaphthalenetetracarboximide. Among the preferred compounds are N-hydroxyimide compounds derived from alicyclic polycarboxylic anhydrides, particularly those derived from aromatic polycarboxylic anhydrides, for example N-hydroxyphthalimide.

[0099]

Such imide compounds have high oxidizing activity and are capable of promoting an oxidation reaction catalytically even under mild condition. Furthermore, by oxidizing a substrate in the presence of the imide compound and a co-catalyst, a hydroxyl group can be introduced with high efficiency.

[0100]

The co-catalyst includes metal compounds, for

example compounds containing elements of Group 2A of Periodic Table of the Elements, transition metal elements (e.g. Group 3A elements, Group 4A elements, Group 5A elements, Group 6A elements, Group 7A elements, Group 8 elements, Group 1B elements, and Group 2B elements) and elements of Group 3B (boron B, aluminum Al, etc.) of the Periodic Table of Elements.

[0101]

The preferred co-catalyst includes Group 4A elements such as Ti, Zr, etc., Group 5A elements such as V, Group 6A elements such as Cr, Mo, W, etc., Group 7A elements such as Mn, Tc, Re, etc., Group 8 elements such as Fe, Ru, Co, Rh, Ni, etc., and Group 1B elements such as Cu.

[0102]

The co-catalyst may for example be an elemental metal or a hydroxide thereof but, in many instances, metal oxides (double oxides or oxo-acid salts), organic acid salts, inorganic acid salts and halides containing the elements, coordination compounds (complexes) and polyacids (heteropolyacids and isopolyacids) or their salts containing the metal elements are used.

[0103]

The oxidation catalyst comprised of the imide compound or the oxidation catalyst comprising the imide compound and co-catalyst may be a homogeneous system or a heterogeneous system. Moreover, the oxidation catalyst or oxidation catalyst system may be a solid catalyst

comprising a catalytic component supported on a support or carrier.

[0104]

The ratio of the co-catalyst to the imide compound can be selected from the range of, for example, about 0.001 to 10 mols of the co-catalyst relative to 1 mol of the imide compound. In order to maintain the activity level of the oxidation catalyst system high, the amount of the co-catalyst is preferably from an effective amount to 0.1 mol (for example, about 0.001 to 0.1 mol, preferably about 0.005 to 0.08 mol, more preferably about 0.01 to 0.07 mol) relative to 1 mol of the imide compound.

[0105]

The amount of the imide compound relative to 1 mol of the substrate is about 0.001 to 1 mol (0.01 to 100 mol %), preferably about 0.001 to 0.5 mol (0.1 to 50 mol %), more preferably about 0.01 to 0.30 mol.

[0106]

The amount of the co-catalyst relative to 1 mol of the substrate is about 0.0001 mol (0.1 mol %) to 0.5 mol, preferably about 0.001 to 0.3 mol, more preferably about 0.0005 to 0.1 mol (e.g. 0.005 to 0.1 mol), in many instances.

[0107]

The oxygen for use in the oxidation reaction may be active oxygen but it is economically advantageous to use molecular oxygen. The molecular oxygen is not particularly restricted but may be pure oxygen or oxygen

diluted with an inert gas such as nitrogen, helium, argon or carbon dioxide. Not only from the standpoint of workability (handling easiness) and safety but also from economic points of view, the use of air is preferable.

[0108]

The amount of oxygen relative to 1 mol of the substrate is usually not less than about 0.5 mol (e.g. 1 mol or more), preferably about 1 to 100 mols, more preferably about 2 to 50 mols. Oxygen is often used in excess mol relative to the substrate and it is particularly advantageous to carry out the reaction in an atmosphere containing molecular oxygen such as air or oxygen gas.

[0109]

The oxidation reaction is usually carried out in an organic solvent inert to the reaction. The organic solvent that can be used includes but is not limited to organic carboxylic acids such as acetic acid and hydroxycarboxylic acids, nitriles such as acetonitrile, benzonitrile, etc., amides such as formamide, acetamide, dimethylformamide (DMF), dimethylacetamide, etc., alcohols such as t-butanol, t-amyl alcohol, etc., aliphatic hydrocarbons such as hexane, octane, etc., aromatic hydrocarbons such as benzene etc., halogenated hydrocarbons, nitro compounds, esters such as ethyl acetate etc., ethers such as diethyl ether, diisopropyl ether, dioxane, etc., and mixed solvents thereof.

[0110]

When the oxidation reaction is carried out in the presence of a protonic acid, the reaction proceeds smoothly and the objective compound can be obtained with high selectivity and in good yield. The protonic acid may be utilized as the solvent as mentioned above. The protonic acid includes organic acids (e.g. organic carboxylic acids such as formic acid, acetic acid, propionic acid, etc., oxalic acid, hydroxycarboxylic acids such as citric acid, tartaric acid, etc., alkylsulfonic acids such as methanesulfonic acid, ethanesulfonic acid, etc., arylsulfonic acids such as benzenesulfonic acid, p-toluenesulfonic acid, etc.) and inorganic acids (e.g. hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, etc.).

[0111]

The oxidation method using the oxidation catalyst or oxidation catalyst system is characterized in that the oxidation reaction proceeds smoothly even under comparatively mild conditions. The reaction temperature may for example be about 0 to 200°C, preferably about 30 to 150°C, and the reaction is generally conducted at about 50 to 120°C in many instances. This reaction can be conducted at atmospheric or under applied pressure.

[0112]

When the above oxidation reaction is carried out in the presence of a strong acid, an oxo group can be introduced with high efficiency. The strong acid includes not only

sulfuric acid and sulfonic acids mentioned above but also superacids, among others.

[00113]

The introduction of a carboxyl group can be achieved by various reactions but it is advantageous to employ a technique (carboxylation process) similar to the above-described oxidation reaction process using the imide compound (or the imide compound and co-catalyst) as a catalyst except that carbon monoxide and oxygen are used in lieu of oxygen. The carbon monoxide and oxygen may be pure carbon monoxide and oxygen or carbon monoxide and oxygen as diluted with an inert gas beforehand in the same manner as mentioned for the oxidation reaction. As the oxygen source, air may be likewise employed.

[0114]

The proportion of carbon monoxide can be selected from the range of not less than 1 mol (e.g. 1 to 1000 mols) relative to 1 mol of the substrate and is preferably an excess mole, for example about 1.5 to 100 mols (e.g. 2 to 50 mols), more preferably about 2 to 30 mols (e.g. 5 to 25 mols).

[0115]

The amount of oxygen can be selected from within the range of, e.g., 0.5 mols or more (e.g., 1 to 100 mols), preferably 0.5 to 30 mols, and more preferably about 0.5 to 25 mols, relative to 1 mol of the substrate.

[0116]

It is preferable to use a larger amount of carbon monoxide than oxygen. The usual ratio of CO to O<sub>2</sub> is CO/O<sub>2</sub> = about 1/99 to 99/1 (mol %) [e.g. 10/90 to 99/1 (mol %)], preferably about 30/70 to 98/2 (mol %), more preferably about 50/50 to 95/5 (mol %), particularly about 60/40 to 90/10 (mol %).

[0117]

A hydroxymethyl group can be generated by reducing the carboxyl group-introduced substrate with hydrogen or a hydrogenation reducing agent (e.g. sodium boron hydride-Lewis acid, aluminum hydride, lithium aluminum hydride, lithium trialkoxyaluminum hydrides, diborane, etc.).

[0118]

A nitro group can be introduced in the conventional manner, for example by a process using a nitrating agent (e.g. mixed acid of sulfuric acid and nitric acid; nitric acid; nitric acid and an organic acid (e.g. a carboxylic acid such as acetic acid); a nitrate and sulfuric acid; dinitrogen pentoxide, etc.).

[0119]

The preferred nitration process may for example be a nitration process which comprises contacting the substrate with a nitrogen oxide in the presence or absence of the imide compound (or the imide compound and co-catalyst).

[0120]

The nitrogen oxide mentioned above can be expressed by the formula  $N_xO_y$  (wherein x represents an integer of 1 or 2; y represents an integer of 1 to 6).

In the compound of the above formula, when x is equal to 1, y is usually an integer of 1 to 3 and when x is equal to 2, y is usually an integer of 1 to 6.

[0121]

The nitrogen oxide, thus, includes but is not limited to  $N_2O$ ,  $NO$ ,  $N_2O_3$ ,  $NO_2$ ,  $N_2O_4$ ,  $N_2O_5$ ,  $NO_3$  and  $N_2O_6$ . These nitrogen oxides can be used each independently or in a combination of two or more species.

[0122]

The preferred nitrogen oxide includes (1) the nitrogen oxide (particularly  $N_2O_3$ ) produced by reacting at least one nitrogen compound selected from the group consisting of dinitrogen oxide ( $N_2O$ ) and nitrogen monoxide ( $NO$ ) with oxygen or a nitrogen oxide containing  $N_2O_3$  as a main component and (2) nitrogen dioxide ( $NO_2$ ) or a nitrogen oxide containing  $NO_2$  as a main component.

[0123]

The nitrogen oxide  $N_2O_3$  can be easily obtained by reacting  $N_2O$  and/or  $NO$  with oxygen. More specifically, it can be prepared by a process which comprises charging a reactor with nitrogen monoxide and oxygen to give  $N_2O_3$  as a blue-colored liquid. Therefore, instead of preparing  $N_2O_3$  in advance, the nitration reaction may be carried out by introducing  $N_2O$  and/or  $NO$  and oxygen into the reaction

system.

[0124]

Here, the oxygen may be either pure oxygen or oxygen diluted with an inert gas (carbon dioxide, nitrogen, helium, argon, etc.) beforehand. The oxygen source may be air.

[0125]

In the reaction mode using nitrogen dioxide (NO<sub>2</sub>), among the nitrogen oxides, the nitration reaction proceeds smoothly even without coexistence of oxygen. Therefore, the reaction system using NO<sub>2</sub> does not essentially require oxygen, although NO<sub>2</sub> may be used in combination with oxygen.

[0126]

In the above oxidation process using the imide compound (or the imide compound and co-catalyst) as a catalyst, it is advantageous to carry out nitration using a nitrogen oxide (or a nitrogen oxide and oxygen) in lieu of oxygen in otherwise the same manner as the oxidation process described above.

[0127]

The amount of the nitrogen oxide can be selected according to the amount of the nitro group to be introduced, for example from the range of about 1 to 50 mols, preferably about 1.5 to 30 mols, relative to 1 mol of the substrate, and is usually about 2 to 25 mols.

[0128]

When the catalyst comprised of the imide compound is used, the nitration reaction proceeds smoothly even

under comparatively mild conditions. The reaction temperature can be selected according to the kinds of imide compound and substrate, for example from the range of about 0 to 150°C, preferably about 25 to 125°C, more preferably about 30 to 100°C. The nitration reaction can be carried out at atmospheric pressure or under applied pressure.

[0129]

The nitro-group introduced into the substrate can be converted to an amino group by reduction. This reduction reaction can be carried out in the conventional manner, for example in the same manner as the reduction reaction for converting the carbonyl compound (1b) to the hydroxy compound (1c) according to the reaction scheme presented hereinbefore.

[0130]

The hydroxyl group introduced into the substrate can be converted to an alkoxy group in the routine manner, and the carboxyl group can be converted to an alkoxy carbonyl group, a carbamoyl group or an N-substituted carbamoyl group by utilizing the conventional esterification reaction or amidation reaction, for instance. Furthermore, the amino group can be converted to an N-substituted amino group using an alkylating agent or an acylating agent.

[0131]

The compound and polymer having a basic group or an acidic group may form salts. For example, a carboxyl group-containing substrate can be reacted with an organic

base or an inorganic base to give the corresponding salt. An amino group-containing substrate can be reacted with an inorganic acid or an organic acid to give the corresponding salt.

[0132]

The oxidation and other reactions can be carried out in any of batch, semi-batch and continuous modes. After completion of each reaction, the reaction product can be easily isolated and purified by the conventional procedure.

[0133]

[Effects of the Invention]

The acid-responsive compound of the present invention has an alicyclic hydrocarbon group (e.g. an adamantane skeleton) and becomes alkali-soluble upon exposure to light, with the result that it finds application as a photoresist in the formation of fine-line patterns. Furthermore, because it is high in sensitivity and etching resistance (dry etching resistance in particular), fine-line patterns can be formed with good reproducibility and high accuracy. In addition, it contributes to improved adhesion to the substrate and improved stability of the resist solution, thus insuring the formation of fine-line patterns with high accuracy and good reproducibility.

[0134]

[Examples]

Hereinafter, the present invention will be described

in further detail with reference to Examples and Comparative Examples but should by no means be construed as defining the present invention.

[0135]

Example 1

(1) Hydroxylation

To a solution of adamantan-1-yl-ethan-1-one (1 mol) in absolute tetrahydrofuran was added a solution of isopropylmagnesium iodide (iso-C<sub>3</sub>H<sub>7</sub>MgI) (1.2 mols) in absolute diethyl ether dropwise, and the mixture was stirred at 10°C for 6 hours to provide 1-(1-hydroxy-1,2-dimethylpropyl)adamantane.

adamantane.

[0136]

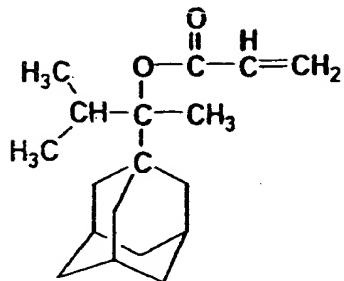
(2) Esterification

A mixture of 1-(1-hydroxy-1,2-dimethylpropyl)adamantane obtained above (1.00 mmol), samarium iodide (SmI<sub>2</sub>) (0.10 mmol), isopropenyl acrylate (1.1 mmols) and dioxane (2 mL) was stirred at 50°C for 6 hours. Analysis by gas chromatography revealed the formation of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane of the following formula (yield 90%) in the reaction mixture.

Mass spectrum: [M] 276, 261, 218, 147, 135.

[0137]

[Formula 10]



[0138]

(3) Polymerization

A monomer mixture (100 parts by weight) of the obtained 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane (50 weight %), methyl methacrylate (10 weight %), butyl acrylate (20 weight %) and methacrylic acid (20 weight %) was polymerized in an organic solvent (toluene) in the presence of polymerization initiator (benzoyl peroxide) (5 parts by weight), and the polymer was precipitated by adding methanol to the reaction mixture. The precipitate was purified by repeating the cycle of dissolution in toluene and precipitation with methanol to provide a copolymer having a weight average molecular weight of about  $1.5 \times 10^4$  (molecular weight in terms of polystyrene according to GPC).

[0139]

Example 2

(1) Hydroxylation

A mixture of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane (10 mmols), NHPI (2 mmols), acetylacetone cobalt ( $\text{Co}(\text{AA})_2$ ) (0.1 mmol) and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6

hours to provide 1-hydroxy-3-(1-acryloyloxy-1,2-dimethylpropyl)adamantane of the following formula (yield 78%).

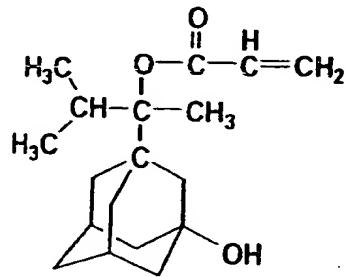
[0140]

Mass spectrum of hydroxyl group-containing compound:

[M] 292, 277, 233, 162, 145, 133.

[0141]

[Formula 11]



[0142]

(2) Polymerization

Using 1-hydroxy-3-(1-acryloyloxy-1,2-dimethylpropyl)adamantane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, Step (3) of Example 1 was otherwise repeated to provide a copolymer.

[0143]

Example 3

(1) Introduction of a carboxyl group

To acetic acid (25 ml) were added adamantan-1-yl-ethan-1-one (1-acetyladamantane) (10 mmols), NHPI (1 mmol) and Co(AA)<sub>2</sub> (0.005 mmol), and the mixture was stirred at 60°C for 6 hours in reactor with a gas pack inflated with

a mixed gas (a mixed gas of carbon monoxide (2 L) and oxygen (0.5 L); pressure: 5 kg/cm<sup>2</sup>). As a result, 1-carboxyadamantan-3-yl-ethan-1-one was obtained at a conversion rate of 78% (yield 62%).

[0144]

(2) Hydroxylation

Using 1-carboxyadamantan-3-yl-ethan-1-one in lieu of adamantan-1-yl-ethan-1-one, Step (1) of Example 1 was otherwise repeated to provide 1-carboxy-3-(1-hydroxy-1,2-dimethylpropyl)adamantane (yield 60%).

[0145]

(3), (4) Esterification and polymerization

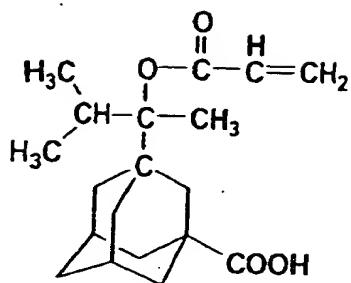
Using 1-carboxy-3-(1-hydroxy-1,2-dimethylpropyl)adamantane in lieu of 1-(1-hydroxy-1,2-dimethylpropyl)adamantane, Steps (2) and (3) of Example 1 were otherwise repeated to provide the carboxyl group-containing compound of the following formula, namely 1-carboxy-3-(1-acryloyloxy-1,2-dimethylpropyl)adamantane [i.e. 1-carboxy-3-(2-acryloyloxy-3-methyl-2-yl)adamantane] (yield 82%), and a copolymer.

[0146]

Mass spectrum of carboxyl group-containing compound: [M] 320, 305, 262, 191, 146, 134.

[0147]

[Formula 12]



[0148]

Example 4

(1) Hydroxylation

Using adamantanone in lieu of adamantan-1-yl-ethan-1-one, Step (1) of Example 1 was otherwise repeated to provide 2-isopropyl-2-hydroxyadamantane at the conversion rate of 76% (yield 61%).

[0149]

(2), (3) Esterification and polymerization

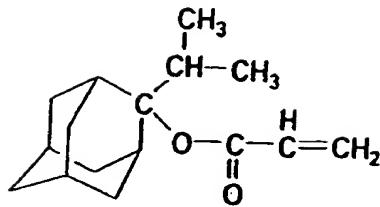
Using 2-isopropyl-2-hydroxyadamantane in lieu of 1-(1-hydroxy-1,2-dimethylpropyl)adamantane, Steps (2), (3) of Example 1 were otherwise repeated to provide the hydroxyl group-containing compound of the following formula, namely 2-isopropyl-2-acryloyloxyadamantane (yield 78%), and a copolymer.

[0150]

Mass spectrum of hydroxyl group-containing compound: [M] 248, 233, 218, 205, 183, 139.

[0151]

[Formula 13]



[0152]

Example 5

(1) Hydroxylation

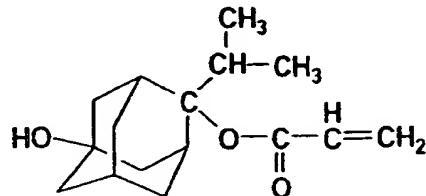
Using 2-isopropyl-2-acryloyloxyadamantane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, the hydroxylation step (Step 2) of Example 2 was otherwise repeated to provide 1-hydroxy-4-isopropyl-4-acryloyloxyadamantane of the following formula (yield 56%).

[0153]

Mass spectrum of hydroxyl group-containing compound: [M] 264, 246, 231, 216, 203, 176, 132.

[0154]

[Formula 14]



[0155]

(3) Polymerization

Using 1-hydroxy-4-isopropyl-4-acryloyloxyadamantane in lieu of 1-(1-acryloyloxy-1,2-

dimethylpropyl)adamantane, Step (3) of Example 1 was otherwise repeated to provide a copolymer.

[0156]

Example 6

(1) Introduction of a carboxyl group

Using adamantanone in lieu of adamantan-1-yl-ethan-1-one, the carboxylation step (Step 1) of Example 3 was otherwise repeated to provide 1-carboxyadamantan-4-one.

[0157]

Using 1-carboxyadamantan-4-one in lieu of adamantan-1-yl-ethan-1-one, Step (1) of Example 1 was otherwise repeated to provide 1-carboxy-4-hydroxy-4-isopropyladamantane (yield 58%).

[0158]

(2), (3) Esterification and polymerization

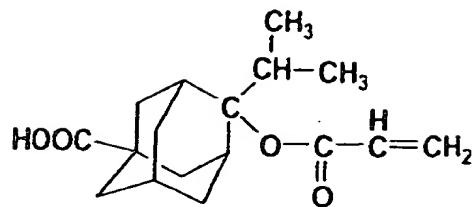
Using 1-carboxy-4-hydroxy-4-isopropyladamantane in lieu of 1-(1-hydroxy-1,2-dimethylpropyl)adamantane, Steps (2) and (3) of Example 1 were otherwise repeated to provide the carboxyl group-containing compound of the following formula, namely 1-carboxy-4-acryloyloxy-4-isopropyladamantane (yield 81%), and a copolymer.

[0159]

Mass spectrum of carboxyl group-containing compound: [M] 292, 221, 206, 191, 178, 133.

[0160]

[Formula 15]



[0161]

Example 7

(1) Hydroxylation

A mixture of 1-acetyladamantane (10 mmols), NHPI (2 mmols), acetylacetonecobalt ( $\text{Co}(\text{AA})_2$ ) (0.1 mmol) and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6 hours, whereby 1-hydroxy-3-acetyladamantane was obtained (yield 80%).

[0162]

(2) Reduction

A mixture of 1-hydroxy-3-acetyladamantane (2 mmols), sodium boron hydride ( $\text{NaBH}_4$ ) (2.4 mmols) and tetrahydrofuran (25 ml) was stirred at room temperature for 3 hours. As a result, 1-hydroxy-3-(1-hydroxyethyl)adamantane was obtained (yield 95%).

[0163]

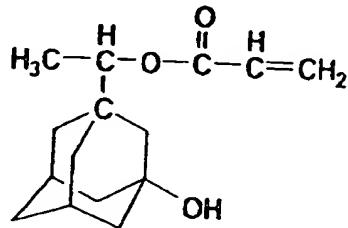
(3) Esterification and polymerization

A mixture of 1-hydroxy-3-(1-hydroxyethyl)adamantane (1 mmol), acryloyl chloride (1.2 mols), triethylamine (1.2 mols) and dioxane (10 ml) was stirred at 40°C for 3 hours. As a result, 1-hydroxy-3-(1-acryloyloxyethyl)adamantane of the following formula

was obtained (yield 78%).

[0164]

[Formula 16]



[0165]

Using 1-hydroxy-3-(1-acryloyloxyethyl)adamantane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, the polymerization step of Example 1 was otherwise repeated to provide a copolymer.

[0166]

Example 8

(1.) Hydroxylation

To a solution of adamantanecarbonyl chloride (1 mol) in absolute tetrahydrofuran was added a solution of ethylmagnesium iodide ( $C_2H_5MgI$ ) (2.2 mols) in absolute diethyl ether dropwise, and the mixture was stirred at room temperature for 6 hours to provide 1-(3-hydroxypent-3-yl)adamantane (yield 95%).

[0167]

Mass spectrum:  $[M]$  222, 204, 193, 175, 161, 147, 135.

[0168]

A mixture of 1-(3-hydroxypent-3-yl)adamantane (10 mmols), NHPI (2 mmols), acetylacetone cobalt ( $Co(AA)_2$ )

(0.1 mmol) and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6 hours. As a result, 1-hydroxy-3-(3-hydroxypent-3-yl)adamantane was obtained (yield 80%).

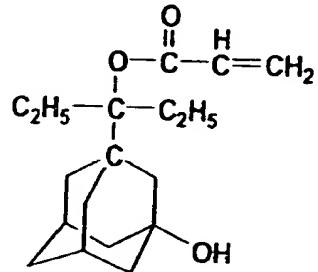
[0169]

(2) Esterification and polymerization

A mixture of 1-hydroxy-3-(3-hydroxypent-3-yl)adamantane (1 mmol), acryloyl chloride (1.2 mols), triethylamine (1.2 mols) and dioxane (10 ml) was stirred at 40°C for 3 hours. As a result, 1-hydroxy-3-(3-acryloyloxy pent-3-yl)adamantane of the following formula was obtained (yield 45%).

[0170]

[Formula 17]



[0171]

Using 1-hydroxy-3-(3-acryloyloxy pent-3-yl)adamantane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, the polymerization step of Example 1 was otherwise repeated to provide a copolymer.

[0172]

Example 9

(1) Hydroxylation

To a solution of adamantanecarbonyl chloride (1 mol) in absolute tetrahydrofuran was added a solution of ethylmagnesium iodide ( $C_2H_5MgI$ ) (1.1 mol) in absolute diethyl ether dropwise, and the mixture was stirred at room temperature for 6 hours to provide 1-(1-hydroxypropyl)adamantane (yield 80%).

[0173]

Mass spectrum: [M] 194, 176, 165, 147, 135.

[0174]

A mixture of 1-(1-hydroxypropyl)adamantane (10 mmols), NHPI (2 mmols), acetylacetonatocobalt ( $Co(AA)_2$ ) (0.1 mmol) and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6 hours. As a result, 1-hydroxy-3-(1-oxopropyl)adamantane was obtained (yield 80%).

[0175]

A mixture of 1-hydroxy-3-(1-oxopropyl)adamantane (2 mmols), sodium boron hydride ( $NaBH_4$ ) (2.4 mmols) and tetrahydrofuran (25 ml) was stirred at room temperature for 3 hours. As a result, 1-hydroxy-3-(1-hydroxypropyl)adamantane was obtained (yield 95%).

[0176]

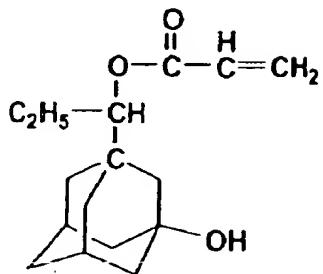
(2) Esterification and polymerization

A mixture of 1-hydroxy-3-(1-hydroxypropyl)adamantane (1 mmol), acryloyl chloride (1.2 mols), triethylamine (1.2 mols) and dioxane (10 ml) was stirred at 40°C for 3 hours. As a result, 1-hydroxy-3-

(1-acryloyloxypropyl)adamantane of the following formula was obtained (yield 75%).

[0177]

[Formula 18]



[0178]

Using 1-hydroxy-3-(1-acryloyloxypropyl)adamantane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, the polymerization step of Example 1 was otherwise repeated to provide a copolymer.

[0179]

Example 10

(1) Hydroxylation

A mixture of adamantane-1-carboxylic acid (10 mmols), NHPI (2 mmols), acetylacetone cobalt ( $\text{Co}(\text{AA})_2$ ) (0.1 mmol) and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6 hours. As a result, 1-hydroxy-3-carboxyadamantane was obtained (yield 80%).

[0180]

(2) Reduction

A mixture of 1-hydroxy-3-carboxyadamantane (2 mmols), sodium boron hydride ( $\text{NaBH}_4$ ) (6 mmols) and tetrahydrofuran (25 ml) was stirred at room temperature

for 6 hours. As a result, 1-hydroxy-3-hydroxymethyladamantane was obtained (yield 90%).

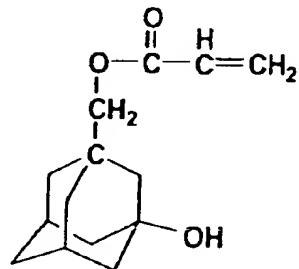
[0181]

(3) Esterification and polymerization

A mixture of 1-hydroxy-3-hydroxymethyladamantane (1 mmol), acryloyl chloride (1.2 mols), triethylamine (1.2 mols) and dioxane (10 ml) was stirred at 40°C for 3 hours. As a result, 1-hydroxy-3-(acryloyloxymethyl)adamantane of the following formula was obtained (yield 90%).

[0182]

[Formula 19]



[0183]

Using 1-hydroxy-3-(acryloyloxymethyl)adamantane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, the polymerization step of Example 1 was otherwise repeated to provide a copolymer.

[0184]

Example 11

(1) Hydroxylation

A mixture of decalin (10 mmols), NHPI (2 mmols), acetylacetone cobalt ( $\text{Co}(\text{AA})_2$ ) (0.1 mmol) and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6

hours. As a result, 9,10-dihydroxy-bicyclo[4.4.0]decane was obtained (yield 70%).

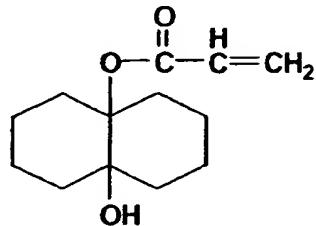
[0185]

(2) Esterification and polymerization

A mixture of 9,10-dihydroxy-bicyclo[4.4.0]decane (1 mmol), acryloyl chloride (1.2 mols), triethylamine (1.2 mols) and dioxane (10 ml) was stirred at 40°C for 3 hours. As a result, 9-hydroxy-10-acryloyloxy-bicyclo[4.4.0]decane of the following formula was obtained (yield 90%).

[0186]

[Formula 20]



[0187]

Using 9-hydroxy-10-acryloyloxy-bicyclo[4.4.0]decane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, the polymerization step of Example 1 was otherwise repeated to provide a copolymer.

[0188]

Example 12

(1) Hydroxylation

A mixture of tricyclo[5.2.1.0<sup>2,6</sup>]decane (10 mmols), NHPI (2 mmols), acetylacetone cobalt (Co(AA)<sub>2</sub>) (0.1 mmol)

and acetic acid (25 ml) was stirred in an oxygen atmosphere at 75°C for 6 hours. As a result, 2,6-dihydroxy-tricyclo[5.2.1.0<sup>2,6</sup>]decane was obtained (yield 70%).

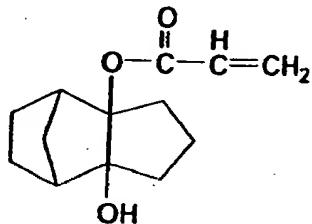
[0189]

(2) Esterification and polymerization

A mixture of 2,6-dihydroxy-tricyclo[5.2.1.0<sup>2,6</sup>]decane (1 mmol), acryloyl chloride (1.2 mols), triethylamine (1.2 mols) and dioxane (10 ml) was stirred at 40°C for 3 hours. As a result, 2-hydroxy-6-acryloyloxy-tricyclo[5.2.1.0<sup>2,6</sup>]decane of the following formula was obtained (yield 70%).

[0190]

[Formula 21]



[0191]

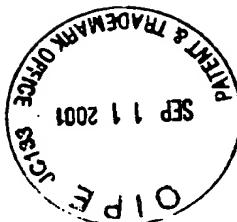
Using 2-hydroxy-6-acryloyloxy-tricyclo[5.2.1.0<sup>2,6</sup>]decane in lieu of 1-(1-acryloyloxy-1,2-dimethylpropyl)adamantane, the polymerization step of Example 1 was otherwise repeated to provide a copolymer.

[0192]

[Photoresist resin composition]

A photoresist resin composition was prepared by mixing 100 parts by weight of each polymer obtained and

15 parts by weight of triphenylphosphoniumhexafluoroantimony with the solvent toluene. This photoresist resin composition was coated on a silicon wafer by the spin coating technique to form a 1.0  $\mu\text{m}$  thick photosensitive layer. After prebaking on a hot plate at 60°C for 100 seconds, exposure was carried out at an illuminating amount 100  $\text{mJ}/\text{cm}^2$  using a KrF excimer stepper, followed by postbaking at 100°C for 60 seconds. Development was then carried out with an aqueous alkaline solution (Tokyo Oka K.K., NMD-3) for 60 seconds and the wafer was rinsed with pure water. As a result, a predetermined pattern could be formed.



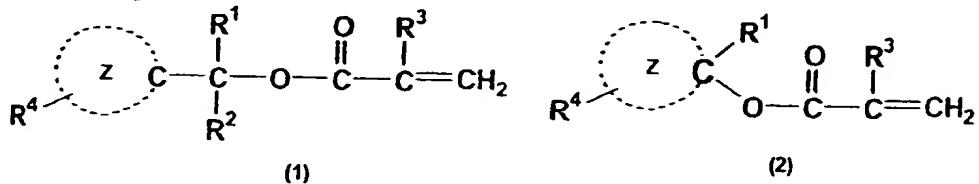
[ Document Name ] ABSTRACT

[Abstract] To provide a photoresist resin composition which is high in etching resistance, solubilizable by irradiation, and capable of providing a finer line pattern.

[Object]

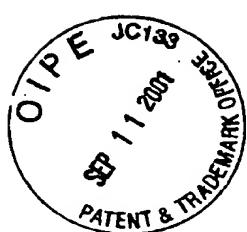
[Means to Solve the Problem(s)] The photoresist resin composition comprises a polymer containing an acid-responsive compound unit of the following formula (e.g. an adamantane skeleton) and a photoactive acid precursor.  $R^1$  may be an alkyl group having a tertiary carbon atom in the 1-position and the Z ring is a bridged-ring hydrocarbon ring comprising 2 to 4 rings.

[Formula 1]



wherein R<sup>1</sup> and R<sup>2</sup> are the same or different from each other and each represents hydrogen atom, an alkyl group or a cycloalkyl group; R<sup>3</sup> represents hydrogen atom or methyl group; R<sup>4</sup> represents a halogen atom, an alkyl group, an oxygen-containing group, amino group or an N-substituted amino group; the Z ring represents a monocyclic or polycyclic alicyclic hydrocarbon ring; in the formula (1), R<sup>1</sup> and R<sup>2</sup> may, jointly and together with the adjacent carbon atom, form an alicyclic hydrocarbon ring.

[Selected Fig.] none



- 1 -

[Document Name] Official Correction Data

[Corrected Document] Petition of Patent

**<Acknowledged Information · Additional Information>**

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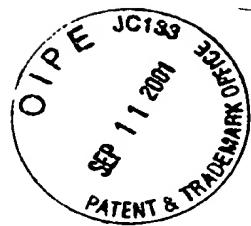
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- 1 -

### Applicant Record

Identification No. [000002901]

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[Reason of Alteration] new registration

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日本国特許庁  
PATENT OFFICE  
JAPANESE GOVERNMENT

別紙添付の書類に記載されている事項は下記の出願書類に記載されている事項と同一であることを証明する。

This is to certify that the annexed is a true copy of the following application as filed with this Office.

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Application Number:

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出願人  
Applicant(s):

ダイセル化学工業株式会社

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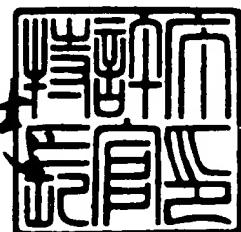
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COMPLIANCE WITH RULE 17.1(a) OR (b)

1999年 6月11日

特許長官  
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Patent Office

佐山 建



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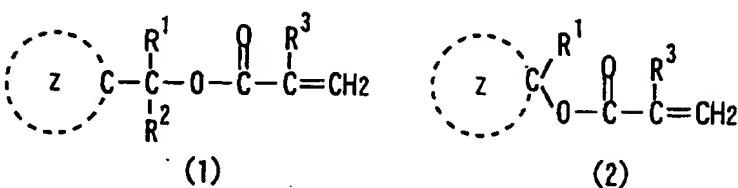
【書類名】 明細書

【発明の名称】 酸感応性化合物及びフォトレジスト用樹脂組成物

### 【特許請求の範囲】

【請求項 1】 下記式 (1) 又は (2)

〔化1〕



(式中、 $R^1$  は第3炭素原子を有する分岐鎖状アルキル基又はシクロアルキル基、 $R^2$  は水素原子又はアルキル基、 $R^3$  は水素原子又はメチル基、環乙は置換基を有していてもよい単環又は多環式脂環族炭化水素環を示す)

で表される酸感応性化合物。

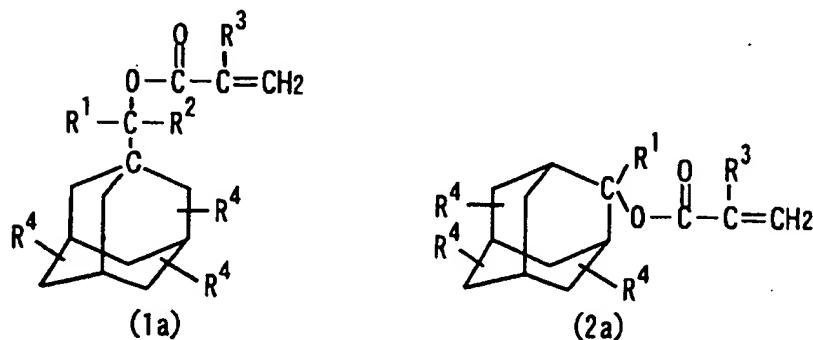
【請求項 2】  $R^1$  が 1 一位に第 3 炭素原子を有する請求項 1 記載の酸感応性化合物。

【請求項3】  $R^1$  が  $1-C_{1-2}$  アルキル- $C_{1-4}$  アルキル基である請求項1記載の酸感応性化合物。

【請求項4】 環乙が、2～4の環を含む架橋環式炭化水素環である請求項1記載の酸感応性化合物。

【請求項5】 下記式(1a)又は(2a)

〔化2〕

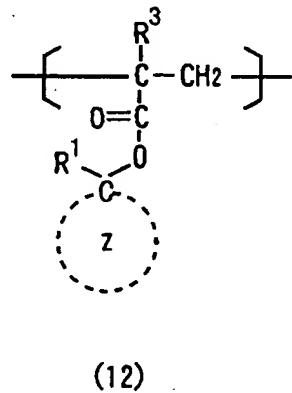
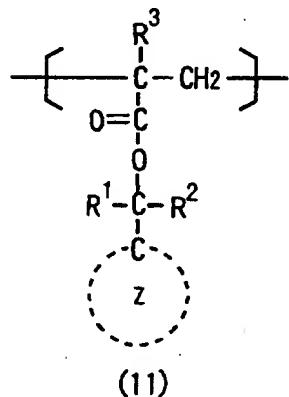


(式中、R<sup>4</sup>は、同一又は異なって、水素原子、ハロゲン原子、アルキル基、オキソ基、ヒドロキシル基、アルコキシ基、カルボキシル基、アルコキシカルボニル基、ヒドロキシメチル基、カルバモイル基、N-置換カルバモイル基、ニトロ基、アミノ基、N-置換アミノ基を示し、これらの基は保護基で保護されていてもよい。R<sup>1</sup>、R<sup>2</sup>、R<sup>3</sup>は前記に同じ)

で表される請求項1記載の酸感応性化合物。

【請求項6】 少なくとも下記式(11)又は(12)で表される単位を有する重合体と光酸発生剤とで構成されているフォトレジスト用樹脂組成物。

【化3】



(式中、R<sup>1</sup>、R<sup>2</sup>、R<sup>3</sup>および環Zは前記に同じ)

【請求項7】 重合体が、共重合体である請求項6記載のフォトレジスト用樹脂組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】

本発明は、アダマンタン誘導体などの酸感応性化合物、およびこの酸感応性化合物を用いたフォトレジスト用樹脂組成物に関する。特に、紫外線や遠紫外線(エキシマーレーザーなどを含む)などを用いてパターン(半導体の微細加工など)を形成するのに適したフォトレジスト用樹脂組成物およびそのための酸感応性化合物に関する。

【0002】

## 【従来の技術】

半導体集積回路の形成には、基板にレジスト薄膜を形成し、パターン露光により潜像を形成した後、現像によりレジストパターンを形成し、このパターンをマスクとしてドライエッチングし、レジストを除去することにより所定のパターンを形成するリソグラフィ技術が利用されている。

## 【0003】

半導体の製造用レジストとして、アルカリ可溶性ノボラック樹脂とジアゾナフトキノン誘導体とを含有する感光性樹脂組成物が知られている。この樹脂組成物は、光照射によりジアゾナフトキノン基が分解してカルボキシル基を生成し、アルカリ不溶性からアルカリ可溶性となることを利用して、ポジ型レジストとして利用されている。また、光照射により不溶化するレジストとして、アジド類による光架橋や、光重合開始剤による光重合を利用したネガ型レジストも知られている。

一方、リソグラフィ技術においては、パターンの微細化により、g線、i線などの紫外光線から、より短波長の露光源、例えば、遠紫外線、真空紫外線、エキシマレーザー光線、電子線、X線などの放射線が利用されている。

しかし、これらのレジストは、樹脂が芳香環を含んでいるため200nm以下の波長に対しては不透明な場合があり、波長193nmのArFエキシマレーザーを用いたフォトレジストの組成物としては適当でない。

## 【0004】

短波長の露光源（ArFエキシマレーザーなど）に適したフォトレジストとして、特開平9-73173号公報には、アダマンタン、ノルボルナンなどの脂環式炭化水素基で保護され、かつ酸により脱離してアルカリ可溶性となる構造単位を有する重合体と、酸発生剤とで構成されたレジスト材料が開示されている。この文献には、前記重合体として、①2-メチル-2-アダマンチル（メタ）アクリレートの共重合体、②2-（1-アダマンチル）プロピル（メタ）アクリレートの共重合体などが例示されている。この重合体は、環内に二重結合を有していないため、上記ArFエキシマレーザー光に対して透明であり、半導体の微細加工において、プラズマガスによるドライエッチング耐性が向上する。

【0005】

しかし、前記重合体と酸発生剤とで構成されたレジストを用いてパターンを形成すると、パターンの微細化に伴ってクラックやパターンの剥離が生じ易くなり、安定して微細パターンを形成できない場合がある。

【0006】

【発明が解決しようとする課題】

従って、本発明の目的は、脂環族炭化水素基（アダマンタン骨格など）を有し、光照射によりアルカリ可溶性重合体を生成でき、微細なパターンを形成するのに有用な酸感応性化合物、およびそれを用いたフォトレジスト用樹脂組成物を提供することにある。

本発明の他の目的は、感度および耐エッチング性（特に耐ドライエッチング性）が高く、微細なレジストパターンを安定かつ高い精度で形成するのに有用な酸感応性化合物、およびそれを用いたフォトレジスト用樹脂組成物を提供することにある。

本発明のさらに他の目的は、基板に対する密着性が高く、高い精度で微細なレジストパターンを安定して形成するのに有用な酸感応性化合物、およびそれを用いたフォトレジスト用樹脂組成物を提供することにある。

【0007】

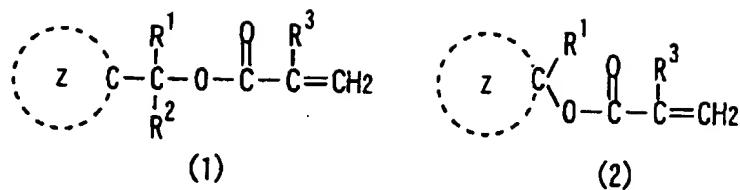
【課題を解決するための手段】

本発明者らは、前記目的を達成するため銳意検討の結果、脂環式炭化水素基とともに特定の構造を有する酸感応性化合物の単位を含む重合体と、光酸発生剤とを組み合わせると、光照射に伴って酸発生剤から生成する酸により重合体から前記脂環式炭化水素基が安定かつ効率よく脱離して、水又はアルカリ現像できるこを見いだし、本発明を完成した。

すなわち、本発明の酸感応性化合物は、下記式（1）又は（2）

【0008】

【化 4】

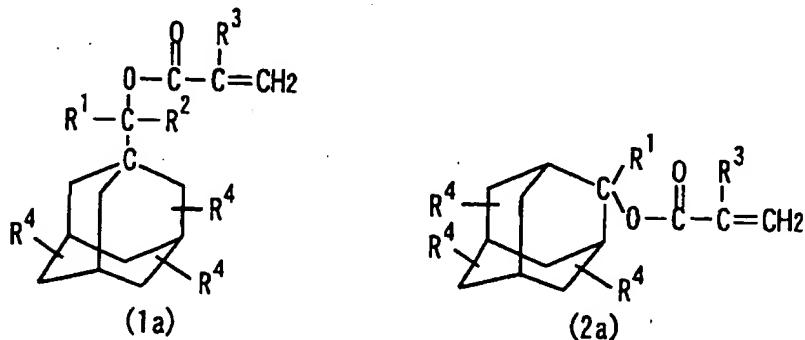


(式中、 $R^1$  は第3炭素原子を有する分岐鎖状アルキル基、又はシクロアルキル基、 $R^2$  は水素原子又はアルキル基、 $R^3$  は水素原子又はメチル基、環乙は置換基を有していてもよい単環又は多環式脂環族炭化水素環を示す)  
で表される。

この酸感応性化合物において、R<sup>1</sup> は  $\alpha$  - 位置 (1 - 位) にメチル炭素原子 (第3炭素原子) を有するアルキル基 (例えば、1 - C<sub>1-2</sub> アルキル - C<sub>1-4</sub> アルキル基など)、環乙は、2 ~ 4 の環を含む架橋環式炭化水素環 (例えば、アダマンタン環など) であってもよい。このような化合物には、例えば、下記式 (1a) 又は (2a) で表されるアダマンタン誘導体が含まれる。

[0009]

【化 5】

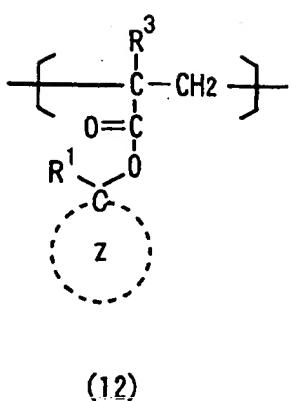
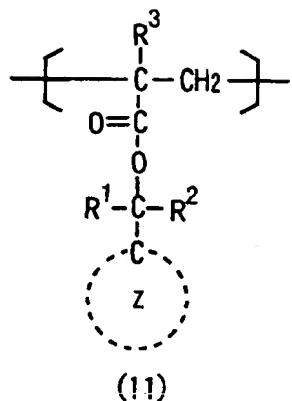


(式中、 $R^4$  は、同一又は異なって、保護基で保護されていてもよい置換基を示し、 $R^1$ 、 $R^2$ 、 $R^3$  は前記に同じ)

本発明のフォトレジスト用樹脂組成物は、少なくとも下記式（11）又は（12）で表される単位を有する重合体と光酸発生剤とで構成できる。

[0010]

【化 6】



(式中、 $R^1$ 、 $R^2$ 、 $R^3$  および環乙は前記に同じ)

[0011]

### 【発明の実施の形態】

前記式(1)(2)(1a)(2a)(11)(12)において、 $R^1$  で表される第3炭素原子を有する分岐鎖状アルキル基としては、例えば、イソプロピル、イソブチル、1-メチルエチル、イソペンチル、1-メチルプロピル(s-ブチル)、1-メチルブチル(s-ペンチル)、s-ヘキシル、1-エチルエチル、1-エチルブチル基などの $1-C_{1-4}$ アルキル- $C_{1-6}$ アルキル基が例示できる。好ましい分枝鎖状アルキル基には、 $R^1$  が  $\alpha$ -位置にメチン炭素原子を有するアルキル基、特に $1-C_{1-2}$ アルキル- $C_{1-4}$ アルキル基(イソプロピル、s-ブチル基など)が含まれる。

【0 0 1 2】

シクロアルキル基としては、例えば、シクロプロピル、シクロブチル、シクロペンチル、シクロヘキシル、シクロヘキシル、シクロオクチル、シクロデシル基などのC<sub>3-10</sub>シクロアルキル基が例示できる。

[0 0 1 3]

$R^2$  で表されるアルキル基には、メチル、エチル基などの  $C_{1-4}$  アルキル基（特にメチル、エチル基）が含まれる。 $R^2$  は、通常、水素原子又はメチル基である。 $R^3$  は水素原子又はメチル基であり、アクリロイル基又はメタクリロイル基を構成する。

## 【0014】

環乙には、種々の脂環族炭化水素環、例えば、単環式炭化水素環、多環式炭化水素環（スピロ炭化水素環、環集合炭化水素環、縮合環式炭化水素環や架橋環式炭化水素環）が含まれる。単環式炭化水素環には、例えば、シクロヘプタン、シクロヘキサン、シクロヘキサン、シクロオクタンなどのC<sub>4-10</sub>シクロアルカン環が含まれ、スピロ炭化水素環には、例えば、スピロ[4.4]ノナン、スピロ[4.5]デカン、スピロビシクロヘキサンなどのC<sub>8-16</sub>炭化水素環などが含まれる。環集合炭化水素環としては、例えば、ビシクロヘキサン、ビパヒドロナフタレン環などのC<sub>5-12</sub>シクロアルカン環を有する炭化水素環が例示でき、縮合環式炭化水素環には、例えば、パヒドロナフタレン環（デカリン環）、パヒドロアントラセン環、パヒドロフェナントレン環、パヒドロアセナフテン環、パヒドロフルオレン環、パヒドロインデン環、パヒドロフェナレン環などの5～8員シクロアルカン環が縮合した縮合環が例示できる。

## 【0015】

好ましい環乙は架橋環式炭化水素環であり、架橋環式炭化水素環には、例えば、ピナン、ボルナン、ノルピナン、ノルボルナンなどの2環式炭化水素類；ホモブレダン、アダマンタン、トリシクロ[5.2.1.0<sup>2,6</sup>]デカン、トリシクロ[4.3.1.1<sup>2,5</sup>]ウンデカンなどの3環式炭化水素類；テトラシクロ[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]ドデカン、パヒドロ-1,4-メタノ-5,8-メタノナフタレンなどの4環式炭化水素類など]、ジエン類の二量体の水素添加物〔例えば、シクロペニタジエン、シクロヘキサジエン、シクロペプタジエンなどのシクロアルカジエンの二量体の水素添加物（例えば、パヒドロ-4,7-メタノインデンなど）、ブタジエンの二量体（ビニルシクロヘキセン）やその水素添加物、ブタジエンとシクロペニタジエンとの二量体（ビニルノルボルネン）やその水素添加物など〕などが含まれる。好ましい架橋環式炭化水素環は、通常、ボルナン、ノルボルナンやアダマンタン骨格を有している。

好ましい環乙は、2～4の環を含む架橋環式炭化水素環である。

## 【0016】

これらの環乙（単環又は多環式脂環族炭化水素環）は置換基を有していてもよ

い。環乙の置換基  $R^4$  としては、水素原子、ハロゲン原子（臭素、塩素、フッ素原子など）、アルキル基（メチル、エチル、ブチル、 $t$ -ブチル基などの  $C_{1-4}$  アルキル基）、オキソ基、ヒドロキシル基、アルコキシ基（メトキシ、エトキシ、 $t$ -ブトキシ基などの  $C_{1-4}$  アルコキシ基）、カルボキシル基、アルコキシカルボニル基（メトキシカルボニル、エトキシカルボニル、ブトキシカルボニル、 $t$ -ブトキシカルボニル基などの  $C_{1-4}$  アルコキシカルボニル基）、ヒドロキシメチル基、カルバモイル基、 $N$ -置換カルバモイル基（ $N-C_{1-4}$  アルキルカルバモイル基など）、ニトロ基、アミノ基、 $N$ -置換アミノ基（モノ又はジ  $C_{1-4}$  アルキルアミノ基など）などが例示できる。

## 【0017】

これらの置換基  $R^4$  は保護基で保護されていてもよく、保護基は酸により脱離可能な保護基、すなわち露光前に重合体が溶解するのを阻止するための溶解阻止修飾基として機能する保護基であってもよい。

ヒドロキシル基およびヒドロキシメチル基の保護基としては、例えば、アルコキシカルボニル基（メトキシカルボニル、エトキシカルボニル、 $t$ -ブトキシカルボニル基などの  $C_{1-4}$  アルコキシカルボニル基）、ベンジルオキシ基などが例示できる。

カルボキシル基の保護基としては、例えば、アルコキシ基（メトキシ、エトキシ、 $t$ -ブトキシ基などの  $C_{1-4}$  アルコキシ基）、アラルキルオキシ基（ベンジルオキシ基、 $p$ -メトキシベンジルオキシ、ジフェニルメチルオキシ、ベンズヒドリルオキシ基など）、 $N$ -ヒドロキシスクシンイミド基などが利用できる。

## 【0018】

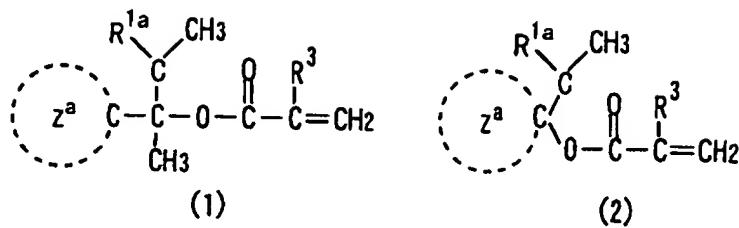
なお、これらの置換基  $R^4$  が、ヒドロキシル基、カルボキシル基、ヒドロキシメチル基、カルバモイル基、アミノ基など（特にヒドロキシル基、カルボキシル基）である場合、レジストと基板との密着性を改善できる。

## 【0019】

好ましい酸感応性化合物には、下記式で表される（メタ）アクリル酸エステルが含まれる。

## 【0020】

【化 7】

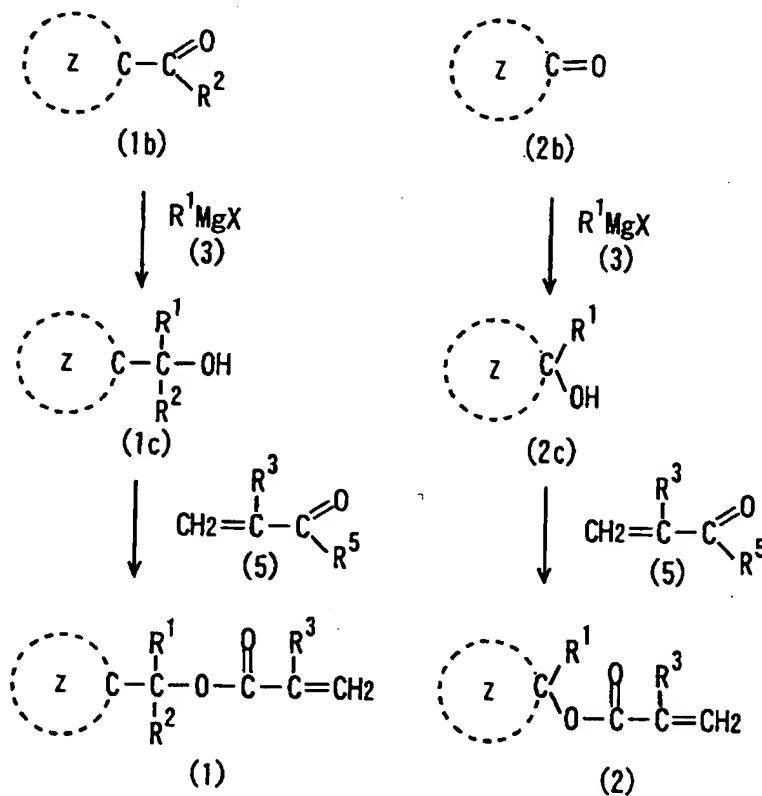


(式中、 $R^1$  は  $C_{1-3}$  アルキル基、 $R^3$  は水素原子又はメチル基、環  $Z^a$  は置換基を有していてもよい架橋環式脂環族炭化水素環を示す)

本発明の酸感応性化合物(1) (2)は、例えば、下記反応工程式に従って調製できる。

[0021]

〔化 8〕



(式中、Xはハロゲン原子、R<sup>5</sup>はハロゲン原子、ヒドロキシル基、アルコキシ基、アルケニルオキシ基、又はアルキニルオキシ基を示す。R<sup>1</sup>、R<sup>2</sup>、R<sup>3</sup>、環Zは前記に同じ)。

ハロゲン原子には、塩素原子、臭素原子、ヨウ素原子などが含まれ、アルコキシ基には、C<sub>1-10</sub>アルコキシ基（例えば、メトキシ、エトキシ、t-ブトキシ基など）が含まれる。アルケニルオキシ基には、C<sub>2-10</sub>アルケニルオキシ基（ビニルオキシ、アリルオキシ、1-プロペニルオキシ、イソプロペニルオキシ、1-ブテニルオキシ、2-ブテニルオキシ、3-ブテニルオキシ、2-ペンテニルオキシ基など）などが含まれ、アルキニルオキシ基には、C<sub>2-10</sub>アルキニルオキシ基（エチニルオキシ、プロピニルオキシ基など）などが含まれる。

## 【0022】

前記反応工程式において、代表的なカルボニル化合物（1b）を例示すると、例えば、单環式化合物（シクロヘキシル-1-エタノンなどのシクロアルキル-1-C<sub>2-6</sub>アルカノンなど）、スピロ環式化合物（スピロ[4.5]デカン-8-イル-1-エタノン、スピロビシクロヘキサン-9-イル-1-エタノンなど）、環集合化合物（ビシクロヘキサン-4-イル-1-エタノンなどのビシクロアルキル-1-C<sub>2-6</sub>アルカノンなど）、縮合環化合物（パーキドロナフチル-1-エタノン、パーキドロフェナントレニル-1-エタノンなど）、架橋環式化合物（ボルナン-2-イル-1-エタノン、ボルナン-3-イル-1-エタノン、ノルボルナン-2-イル-1-エタノンなどの2環式化合物、アダマンタン-1-イル-エタン-1-オン、アダマンタン-1-イル-プロパン-1-オン、アダマンタン-1-イル-ブタン-1-オン、メチルアダマンタン-1-イル-エタン-1-オンなどのアダマンチル-1-C<sub>2-6</sub>アルカノンなどの3環式化合物など）、ジエン類の二量体の水素添加物からの誘導体（パーキドロ-4,7-メタノインデン-1-イル-1-エタノンなどのパーキドロ-4,7-メタノインデニル-1-C<sub>2-6</sub>アルカノン）などが例示できる。

## 【0023】

カルボニル化合物（2b）としては、例えば、单環式ケトン（シクロヘキサノン、メチルシクロヘキサノンなどのシクロアルカノンなど）、スピロ環式ケトン（スピロ[4.5]デカン-8-オン、スピロビシクロヘキサン-9-オンなど）、環集合式ケトン（ビシクロヘキサン-4-オンなどのビシクロアルカノンなど）、縮合環化合物（パーキドロナフタレン-1-オン、パーキドロナフタレン-

2-オン、パーキドロフェナントレン-1-オンなど)、架橋環式化合物(ボルナン-2-オン、ボルナン-3-オン、ノルボルナン-2-オンなどの2環式化合物、アダマンタノン、メチルアダマンタノン、ジメチルアダマンタノンなどの3環式化合物など)、ジエン類の二量体の水素添加物からの誘導体(パーキドロ-4、7-メタノインデン-1-オンなど)などが例示できる。

## 【0024】

前記反応工程式において、カルボニル化合物(1b) (2b) と試薬 $R^1MgX$  (3)との反応は、慣用のグリニヤール反応に準じて行うことができる。グリニヤール試薬 $R^1MgX$  (3)の使用量は、例えば、前記カルボニル化合物(1b) (2b) 1モルに対して、0.8~3モル、好ましくは1~2モル、さらに好ましくは1~1.5モル程度である。反応は、反応に不活性な溶媒、例えば、炭化水素類(ヘキサン、シクロヘキサンなど)、エーテル類(ジメチルエーテル、ジエチルエーテル、テトラヒドロフランなど)などの存在下で行うことができる。反応温度は、例えば、0~100°C、好ましくは10~50°C程度の範囲から適当に選択できる。

## 【0025】

反応により生成したヒドロキシ化合物(1c) (2c) は必要により単離して(メタ)アクリル酸又はその誘導体(5)とのエステル化反応に供することにより、酸感応性化合物(1) (2)を生成させることができる。

## 【0026】

(メタ)アクリル酸又はその誘導体(5)としては、(メタ)アクリル酸、無水(メタ)アクリル酸、脱離基を有する反応性誘導体[例えば、酸ハライド(メタ)アクリル酸クロライド、(メタ)アクリル酸プロマイドなど]、(メタ)アクリル酸アルキルエステル((メタ)アクリル酸メチル、(メタ)アクリル酸エチル、(メタ)アクリル酸プロピル、(メタ)アクリル酸ブチル、(メタ)アクリル酸イソブチル、(メタ)アクリル酸 $\tau$ -ブチルなどの(メタ)アクリル酸C1-6アルキルエステルなど)、(メタ)アクリル酸アルケニルエステル((メタ)アクリル酸ビニル、(メタ)アクリル酸アリル、(メタ)アクリル酸1-プロペニル、(メタ)アクリル酸イソプロペニル、(メタ)アクリル酸1-ブテニル

、(メタ)アクリル酸2-ブテニル、(メタ)アクリル酸3-ブテニル、(メタ)アクリル酸2-ペンテニルなどの(メタ)アクリル酸C<sub>2-10</sub>アルケニルエステルなど)、(メタ)アクリル酸アルキニルエステル((メタ)アクリル酸エチル、(メタ)アクリル酸プロピニルなどの(メタ)アクリル酸C<sub>2-10</sub>アルキニルエステルなど)】などが例示できる。

好ましい化合物(5)には、(メタ)アクリル酸、(メタ)アクリル酸ハライド、(メタ)アクリル酸C<sub>1-6</sub>低級アルキルエステル、(メタ)アクリル酸C<sub>2-6</sub>アルケニルエステル、(メタ)アクリル酸C<sub>2-6</sub>アルキニルエステルが含まれる。特に、(メタ)アクリル酸ハライド、(メタ)アクリル酸C<sub>2-6</sub>アルケニルエステルを用いると、付加重合などの副反応を抑制しつつ、脱離基の交換反応により、高い選択率および収率で対応する酸感応性化合物を生成させることができる。

#### 【0027】

前記エステル化反応は、慣用の方法、例えば、適当な触媒(酸触媒など)の存在下で行ってもよい。なお、(メタ)アクリル酸ハライドを用いると、酸感応性化合物がハロゲン成分で汚染される場合がある。そのため、エステル化反応は、(メタ)アクリル酸を用いるエステル化反応、エステル交換反応を利用するのが好ましい。このようなエステル化反応やエステル交換反応においては、慣用のエステル化触媒(例えば、硫酸などの非ハロゲン系無機酸、塩酸、p-トルエンスルホン酸などのスルホン酸、酸性イオン交換樹脂などのプロトン酸、三フッ化ホウ素などのルイス酸、酵素など)、エステル交換触媒(例えば、上記エステル化触媒、ナトリウムアルコキシドなどのアルカリ金属アコキシド、アルミニウムアルコキシド、チタン酸エステルなど)が利用できる。

#### 【0028】

反応効率を高め、高い収率で酸感応性化合物を得るために、前記ヒドロキシ化合物(1c) (2c)と(メタ)アクリル酸又はその誘導体(5)とのエステル化反応(エステル交換反応などの脱離基交換反応を含む)は、周期表3族元素化合物で構成された触媒の存在下で行うのが有利である。このような触媒を用いる反応では、アミン塩酸塩などの生成を抑制できるとともに、(メタ)アクリル酸C<sub>1-4</sub>

低級アルキルエステル、(メタ)アクリル酸C<sub>2-4</sub>アルケニルエステルを用いると、ハロゲン成分により目的化合物が汚染することがない。さらに、(メタ)アクリル酸又はその誘導体(5)として低沸点化合物(上記エステルなど)が使用できるので、反応後の処理も容易であり、単離収率を大きく改善できる。

## 【0029】

周期表3族化合物で構成された触媒において、周期表3族元素には、例えば、希土類元素〔例えば、スカンジウム、イットリウム、ランタノイド系列元素(ラントン、セリウム、プラセオジム、ネオジム、プロメチウム、サマリウム、ユーロピウム、ガドリニウム、テルビウム、ジスプロシウム、ホルミウム、エルビウム、ツリウム、イッテルビウム、ルテチウム)〕、アクチノイド系列元素(例えば、アクチニウムなど)などが含まれる。好ましい周期表3族元素には、希土類元素、例えば、スカンジウム、イットリウム、ランタノイド系列元素(サマリウム、ガドリニウム、イッテリビウムなど)が含まれる。

## 【0030】

周期表3族元素の原子価は特に制限されず、2価～4価程度、特に2価又は3価である場合が多い。前記周期表3族元素化合物は、触媒活性を有する限り特に制限されず、金属単体、無機化合物(ハロゲン化物、酸化物、複酸化物、リン化合物、窒素化合物など)や有機化合物(有機酸など)との化合物や錯体であってもよく、通常、前記元素を含む水酸化物または酸素酸塩、有機酸塩、無機酸塩、ハロゲン化物、前記金属元素を含む配位化合物(錯体)などである場合が多い。錯体はメタロセン化合物のようなπ錯体であってもよい。さらに、周期表3族元素化合物は他の金属との複合金属化合物であってもよい。これらの触媒は一種又は二種以上使用できる。

## 【0031】

以下に、サマリウム化合物を例にとって触媒成分を具体的に説明するが、サマリウム化合物に対応する他の周期表3族元素化合物も有効に使用できる。

水酸化物には、例えば、水酸化サマリウム(II)、水酸化サマリウム(III)などが含まれ、金属酸化物には、例えば、酸化サマリウム(II)、酸化サマリウム(III)などが含まれる。

有機酸塩としては、例えば、有機カルボン酸（モノカルボン酸、多価カルボン酸）、オキシカルボン酸、チオシアン酸、スルホン酸（アルキルスルホン酸、ベンゼンスルホン酸、アリールスルホン酸など）などの有機酸との塩が例示され、無機酸塩としては、例えば、硝酸塩、硫酸塩、リン酸塩、炭酸塩、過塩素酸塩など挙げられる。有機酸塩又は無機酸塩としては、例えば、酢酸サマリウム、トリクロロ酢酸サマリウム、トリフルオロ酢酸サマリウム、トリフルオロメタンスルホン酸サマリウム（すなわち、サマリウムトリフラーート），硝酸サマリウム、硫酸サマリウム、リン酸サマリウム、炭酸サマリウムなどが例示できる。

ハロゲン化物としては、フッ化物、塩化物、臭化物およびヨウ化物などが例示できる。

### 【0032】

錯体を形成する配位子としては、OH（ヒドロキソ）、アルコキシ基、アシル基、アルコキシカルボニル基、アセチルアセトナト、シクロペントジエニル、C<sub>1-4</sub> アルキル置換シクロペントジエニル（ペントメチルシクロペントジエニルなどのC<sub>1-2</sub> アルキル置換シクロペントジエニルなど）、ジシクロペントジエニル、C<sub>1-4</sub> アルキル置換ジシクロペントジエニル（ペントメチルジシクロペントジエニルなどのC<sub>1-2</sub> アルキル置換ジシクロペントジエニルなど）、ハロゲン原子、CO、CN、酸素原子、H<sub>2</sub>O（アコ）、ホスフィンなどのリン化合物、NH<sub>3</sub>（アンミン）、NO、NO<sub>2</sub>（ニトロ）、NO<sub>3</sub>（ニトラト）、エチレンジアミン、ジエチレントリアミン、ピリジン、フェナントロリンなどの窒素含有化合物などが挙げられる。錯体又は錯塩において、同種又は異種の配位子は一種又は二種以上配位していてもよい。

前記錯体のうち、サマロセン型錯体としては、ジアセチルアセトナトサマリウム（II），トリアセチルアセトナトサマリウム（III），ジシクロペントジエニルサマリウム（II），トリシクロペントジエニルサマリウム（III），ジペントメチルシクロペントジエニルサマリウム（II），トリペントメチルシクロペントジエニルサマリウム（III）などが例示できる。

### 【0033】

なお、周期表3族元素化合物〔電子供与性の高いペントメチルシクロペントジ

エニル配位子を有する2価のサマロセン型錯体  $[(C_5Me_5)_2Sm]$  (PM Sm) ] , サマリウムのハロゲン化合物、アルコキシド、ヒドロキシドなどのサマリウム化合物など] を触媒として用いると、平衡反応として不利なエステル化反応においても、副反応を抑制しつつルイス酸触媒やプロトン酸触媒よりも高い反応効率でエステル化が進行する。そのため、触媒は、エステル交換反応などの脱離基交換反応を利用して、前記酸感応性化合物(1) (2)を生成させる上で有用である。

#### 【0034】

前記周期表3族化合物で構成された触媒は、均一系であってもよく、不均一系であってもよい。また、触媒は、担体に周期表3族化合物で構成された触媒成分が担持された固体触媒であってもよい。担体としては、活性炭、ゼオライト、シリカ、シリカーアルミナ、ベントナイトなどの多孔質担体を用いる場合が多い。触媒成分の担持量は、担体100重量部に対して、周期表3族化合物0.1~50重量部、好ましくは0.5~30重量部、さらに好ましくは1~20重量部程度である。

#### 【0035】

前記触媒(周期表3族元素化合物が構成される触媒など)の使用量は、広い範囲で選択でき、例えば、前記ヒドロキシ化合物(1c) (2c)に対して0.1モル%~1当量、好ましくは0.5~50モル%、さらに好ましくは1~25モル%(例えば、5~20モル%)程度の範囲から適当に選択できる。

#### 【0036】

前記エステル化反応(特に周期表3族化合物を触媒とする反応)は、オキシムの存在下で行ってもよい。オキシムはアルドキシム、ケトキシムのいずれであってもよく、オキシムとしては、例えば、2-ヘキサノンオキシムなどの脂肪族オキシム、シクロヘキサノンオキシムなどの脂環族オキシム、アセトフェノンオキシム、ベンゾフェノンオキシム、ベンジルジオキシムなどの芳香族オキシムなどが例示できる。

オキシムの使用量は、広い範囲で選択でき、例えば、前記ヒドロキシ化合物(1c) (2c)に対して0.1モル%~1当量、好ましくは1~50モル%、さらに

好ましくは5～40モル%（例えば、5～30モル%）程度の範囲から適当に選択できる。

## 【0037】

ヒドロキシ化合物(1c) (2c)と(メタ)アクリル酸又はその誘導体(5)との使用割合は、ヒドロキシ化合物(1c) (2c) 1当量（すなわち、ヒドロキシル基当たりのヒドロキシ化合物の重量）に対して(メタ)アクリル酸又はその誘導体(5) 0.5～5モル、好ましくは0.8～5モル、特に1モル以上（例えば、1～3モル、特に1～1.5モル）程度である。なお、前記エステル化反応は平衡反応であるため、(メタ)アクリル酸又はその誘導体(5)の使用量が多い程、反応を進行させる上で有利であるが、前記周期表3族化合物を触媒とすると、触媒活性が極めて高いため、(メタ)アクリル酸又はその誘導体(5)を大過剰量で使用する必要はない。特に、反応平衡の点から極めて不利な組合せの反応において、(メタ)アクリル酸又はその誘導体(5)としてビニル性脱離基を有する前記アルケニルエステル（ビニルエステルなど）を用いる場合には、むしろ、ヒドロキシ化合物(1c) (2c)の脱離基1当量に対して化合物(1c)を1モル以下の量（例えば、0.4～1モル、好ましくは0.5～1モル）で使用しても、反応が速やかに完結し好成績が得られる場合が多い。

前記触媒を用いる方法では、反応熱の高い(メタ)アクリル酸クロライドなどの酸ハライドを用いる方法に比べて、反応熱が小さいため、溶媒量が少なくても円滑に反応を進行させ、高い収率で目的化合物を生成させることができる。

## 【0038】

前記エステル化反応は、反応に不活性な溶媒の存在下又は非存在下で行なうことができ、反応溶媒としては、例えば、脂肪族炭化水素類、脂環族炭化水素類、芳香族炭化水素類、ケトン類、エーテル類、アミド類、N-メチルピロリドン、ニトリル類などの非プロトン性極性溶媒、およびこれらの混合溶媒などが例示できる。反応溶媒としては、(メタ)アクリル酸又はその誘導体(5)を用いてもよい。

なお、親水性の高いヒドロキシ化合物(1c) (2c)を用いる場合、溶媒としては、親水性溶媒（アセトン、メチルエチルケトンなどのケトン類、ジオキサン、

ジエチルエーテル、テトラヒドロフランなどのエーテル類、非プロトン性極性溶媒)、又は親水性溶媒と疎水性溶媒(脂肪族、脂環族又は芳香族炭化水素類)との混合溶媒を使用してもよい。

## 【0039】

なお、前記反応が平衡反応であるため、反応を促進するためには、脱離成分などの反応阻害成分を反応系外へ速やかに除去するのが有利である。脱離成分を除去するためには、高沸点溶媒(例えば、沸点50~120℃、特に60~115℃程度の有機溶媒)又は共沸性溶媒(例えば、前記炭化水素類など)を用いるのが有利である。

## 【0040】

エステル化反応温度は、例えば、0~150℃、好ましくは25~120℃程度の範囲から選択できる。なお、前記周期表3族元素化合物で構成された触媒を用いると、温和な条件であっても高い効率で酸感応性化合物が生成し、反応温度は、例えば、0~150℃、好ましくは10~100℃、好ましくは20~80℃程度であってもよい。特に、前記(メタ)アクリル酸又はその誘導体(5)として前記アルケニルエステルなどを用いると、20~50℃程度の温和な条件でも反応を円滑に進行させることができる。反応は常圧、減圧又は加圧下で行なうことができる。また、反応は、回分式、半回分式、連続式などの慣用の方法により行なうことができる。

## 【0041】

これらの酸感応性化合物(1)~(2)は、反応終了後、慣用の方法、例えば、濾過、濃縮、蒸留、抽出、晶析、再結晶、カラムクロマトグラフィーなどの分離手段や、これらを組合せた分離手段により、容易に分離精製できる。

## 【0042】

## [フォトレジスト用樹脂組成物]

本発明のフォトレジスト用樹脂組成物の特色は、少なくとも前記式(11)又は(12)で表される単位(アダマンタン骨格を有する単位など)を有する重合体と、光酸発生剤とを組合わせ、光照射により前記重合体を可溶化する点にある。すなわち、バルキーで疎水性の高い環乙に、第3炭素原子を含む分岐鎖状アルキル

基が隣接しており、光照射により生成した酸により、エステル結合が安定かつ効率よく脱離するためか、感度が高く、しかも高い耐エッティング性などを維持しつつ微細なレジストパターンを高い精度で安定に形成できる。

#### 【0043】

前記重合体は、前記式(1) (2)で表される酸感応性化合物の単独又は共重合体であってもよく、前記式(1) (2)で表される酸感応性化合物と共重合体単量体との共重合体であってもよい。

共重合性単量体としては、例えば、(メタ)アクリル系単量体(例えば、(メタ)アクリル酸メチル、(メタ)アクリル酸エチル、(メタ)アクリル酸イソプロピル、(メタ)アクリル酸ブチル、(メタ)アクリル酸s-ブチル、(メタ)アクリル酸t-ブチル、(メタ)アクリル酸ヘキシル、(メタ)アクリル酸オクチル、(メタ)アクリル酸2-エチルヘキシルなどの(メタ)アクリル酸C<sub>1-10</sub>アルキルエステル、(メタ)アクリル酸2-ヒドロキシエチル、(メタ)アクリル酸2-ヒドロキシプロピルなどの(メタ)アクリル酸ヒドロキシC<sub>2-6</sub>アルキルエステル、(メタ)アクリル酸グリシジル、(メタ)アクリロニトリル、(メタ)アクリル酸シクロヘキシル、(メタ)アクリル酸フェニルなど)、スチレン系単量体(スチレン、 $\alpha$ -メチルスチレン、ビニルトルエンなど)、ビニルエスチル系単量体(酢酸ビニル、プロピオン酸ビニルなど)、カルボキシル基含有単量体((メタ)アクリル酸、無水マレイン酸、イタコン酸、マレイン酸モノエステルなど)、スルホン酸基含有単量体(スチレンスルホン酸など)などが例示できる。

#### 【0044】

共重合体における酸感応性化合物(1) (2)の割合は、例えば、10~100重量%(例えば、15~90重量%)、好ましくは25~100重量%(例えば、30~75重量%)、さらに好ましくは30~100重量%(例えば、35~70重量%)程度である。

#### 【0045】

光酸発生剤としては、露光により効率よく酸(プロトン酸やルイス酸)を生成する慣用の化合物、例えば、ジアゾニウム塩、ヨードニウム塩、スルホニウム塩

、オキサチアゾール誘導体、s-トリアジン誘導体、イミド化合物、オキシムスルホネート、ジアゾナフトキノン、スルホン酸エステル〔1-フェニル-1-(4-メチルフェニル)スルホニルオキシ-1-ベンゾイルメタン、1, 2, 3-トリスルホニルオキシメチルベンゼン、1, 3-ジニトロ-2-(4-フェニルスルホニルオキシメチル)ベンゼン、1-フェニル-1-(4-メチルフェニル)スルホニルオキシメチル-1-ヒドロキシ-1-ベンゾイルメタン、ジスルホン誘導体(ジフェニルジスルホンなど)、ベンゾイントシレートなど〕やルイス酸塩(トリフェニルスルホニウムヘキサフルオロアンチモン( $\text{Ph}_3\text{S}^+\text{SbF}_6^-$ )、トリフェニルスルホニウムヘキサフルオロホスフェート( $\text{Ph}_3\text{S}^+\text{PF}_6^-$ )、トリフェニルスルホニウムメタンスルホニル( $\text{Ph}_3\text{S}^+\text{CH}_3\text{SO}_3^-$ )、ジフェニルヨードヘキサフルオロホスフェートなど)などが使用できる。なお、 $\text{Ph}$ はフェニル基を示す。

これらの光酸発生剤は単独で又は二種以上組合わせて使用できる。

#### 【0046】

前記光酸発生剤の使用量は、光照射により生成する酸の強度や酸感応性化合物の使用量などに応じて選択でき、例えば、前記重合体100重量部に対して0.1~30重量部、好ましくは1~25重量部、さらに好ましくは2~20重量部程度の範囲から選択できる。

#### 【0047】

フォトレジスト用樹脂組成物は、アルカリ可溶性樹脂(ノボラック樹脂、フェノール樹脂、カルボキシル基含有樹脂など)などのアルカリ可溶成分、着色剤(染料)、有機溶媒などを含んでいてもよい。有機溶媒としては、例えば、炭化水素類、ハロゲン化炭化水素類、アルコール類、エステル類、ケトン類、エーテル類、セロソルブ類、カルビトール類、グリコールエーテルエステル類(セロソルブアセテートなど)およびこれらの混合溶媒が使用できる。

さらに、フォトレジスト用樹脂組成物は、フィルターなどの慣用の分離精製手段により夾雑物を除去してもよい。

#### 【0048】

本発明のフォトレジスト用樹脂組成物は、前記重合体と光酸発生剤とを混合す

ることにより調製でき、このフォトレジスト用樹脂組成物は、基材又は基板に塗布し、乾燥した後、所定のマスクを介して、塗膜（レジスト膜）に光線を露光して潜像パターンを形成した後、現像することにより、微細なパターンを高い精度で形成でき、光線に対する感度およびパターンの高解像度が高い。

## 【0049】

基材又は基板は、フォトレジスト用樹脂組成物の用途に応じて選択でき、シリコンウェハー、金属、プラスチック、ガラス、セラミックスなどであってもよい。フォトレジスト用樹脂組成物の塗布は、用途に応じた慣用の方法、例えば、スピンドルコーティング、ロールコーティングなどの方法が採用できる。フォトレジスト用樹脂組成物の塗膜の厚みは、例えば、0.1～20μm程度の範囲から適当に選択できる。

## 【0050】

露光には、種々の波長の光線、例えば、紫外線、X線などが利用でき、半導体製造用レジストでは、通常、g線、i線、エキシマーレーザー（例えば、XeC<sub>1</sub>、KrF、KrCl、ArF、ArClなど）などが利用できる。

露光エネルギーは、例えば、1～1000mJ/cm<sup>2</sup>、好ましくは10～500mJ/cm<sup>2</sup>程度の範囲から選択できる。

## 【0051】

光照射により酸発生剤から酸が生成し、生成した酸により環乙を含む基（通常、環乙を含むアルコールとして）が脱離し、可溶化に寄与するカルボキシル基が生成する。そのため、水現像液やアルカリ現像液により現像し、所定のパターンを形成できる。特に、本発明のフォトレジスト用樹脂組成物はアダマンタン骨格などの環乙を有しているので、エッティング（特にドライエッティング）に対する耐性が高く、微細な回路パターンを高い精度で形成できる。なお、環乙を含む基の脱離は、露光とその後のベーキング（Post Exposure Baking, PEB）により促進させてもよい。

本発明は、種々の用途、例えば、回路形成材料（半導体製造用レジスト、プリント配線板など）、画像形成材料（印刷版材、レリーフ像など）などに利用できる。

## 【0052】

## [官能基の導入]

酸感応性化合物(1)(2)や重合体の単位(11)(12)は、前記のように置換基R<sup>4</sup>を有していてもよい。置換基R<sup>4</sup>は、前記反応工程のうち適当な工程又は反応終了後に導入できる。例えば、ヒドロキシル基は、慣用の酸化方法、例えば、硝酸やクロム酸を用いる酸化方法、触媒としてコバルト塩を用いる酸素酸化方法、生化学的酸化方法などにより得ることができ、ハロゲン原子(例えば、臭素原子など)を導入し、硝酸銀や硫酸銀などの無機塩を用いて加水分解してヒドロキシル基を導入する方法により得ることもできる。好ましい方法では、特開平9-327626号公報などに記載されている酸化触媒を用いる方法が含まれる。この酸化方法では、特定のイミド化合物で構成された酸化触媒、又は上記イミド化合物と助触媒とで構成された酸化触媒の存在下、前記式(1a)(2a)(1b)(2b)(1c)(2c)で表される基質化合物や重合体の単位(11)(12)を酸素酸化することによりヒドロキシル基を導入できる。

## 【0053】

前記イミド化合物としては、N-ヒドロキシイミド基を有する化合物(1~3程度のN-ヒドロキシイミド基を有する脂肪族、脂環族、芳香族化合物など)が含まれ、例えば、N-ヒドロキシコハク酸イミド、N-ヒドロキシマレイン酸イミド、N-ヒドロキシヘキサヒドロフタル酸イミド、N, N'-ジヒドロキシシクロヘキサンテトラカルボン酸イミド、N-ヒドロキシフタル酸イミド、N-ヒドロキシテトラブロモフタル酸イミド、N-ヒドロキシテトラクロロフタル酸イミド、N-ヒドロキシヘット酸イミド、N-ヒドロキシハイミック酸イミド、N-ヒドロキシトリメリット酸イミド、N, N'-ジヒドロキシピロメリット酸イミド、N, N'-ジヒドロキシナフタレンテトラカルボン酸イミドなどが挙げられる。好ましい化合物は、脂環族多価カルボン酸無水物、なかでも芳香族多価カルボン酸無水物から誘導されるN-ヒドロキシイミド化合物、例えば、N-ヒドロキシフタル酸イミドなどが含まれる。

## 【0054】

このようなイミド化合物は、酸化活性が高く、温和な条件であっても、酸化反

応を触媒的に促進できる。さらに、前記イミド化合物と助触媒との共存下で基質を酸化すると、高い効率でヒドロキシル基を導入できる。

## 【0055】

助触媒には、金属化合物、例えば、周期表2A族元素、遷移金属元素（例えば、周期表3A族元素、周期表4A族元素、5A族元素、6A族元素、7A族元素、8族元素、1B族元素、2B族元素）や、周期表3B族元素（ホウ素B、アルミニウムA1など）を含む化合物が含まれる。

好ましい助触媒には、Ti, Zrなどの4A族元素、Vなどの5A族元素、Cr, Mo, Wなどの6A族元素、Mn, Tc, Reなどの7A族元素、Fe, Ru, Co, Rh, Niなどの8族元素、Cuなどの1B族元素を含む化合物が含まれる。

## 【0056】

助触媒は、金属単体、水酸化物などであってもよいが、通常、前記元素を含む金属酸化物（複酸化物または酸素酸塩）、有機酸塩、無機酸塩、ハロゲン化物、前記金属元素を含む配位化合物（錯体）やポリ酸（ヘテロポリ酸、イソポリ酸）又はその塩などである場合が多い。

## 【0057】

前記イミド化合物で構成された酸化触媒、又はイミド化合物および前記助触媒で構成される酸化触媒系は、均一系であってもよく、不均一系であってもよい。また、前記酸化触媒又は酸化触媒系は、担体に触媒成分が担持された固体触媒であってもよい。

## 【0058】

イミド化合物に対する助触媒の割合は、例えば、イミド化合物1モルに対して、助触媒0.001~10モル程度の範囲から選択でき、酸化触媒系の高い活性を維持するためには、助触媒の割合は、イミド化合物1モルに対して、有効量以上であって0.1モル以下（例えば、0.001~0.1モル、好ましくは0.005~0.08モル、さらに好ましくは0.01~0.07モル程度）であるのが好ましい。

## 【0059】

前記イミド化合物の使用量は、例えば、基質1モルに対して0.001~1モル(0.01~100モル%)、好ましくは0.001~0.5モル(0.1~50モル%)、さらに好ましくは0.01~0.30モル程度である。

また、助触媒の使用量は、例えば、基質1モルに対して0.0001モル(0.1モル%)~0.5モル、好ましくは0.001~0.3モル、さらに好ましくは0.0005~0.1モル(例えば、0.005~0.1モル)程度である場合が多い。

酸化反応において、酸素は、活性酸素であってもよいが、分子状酸素を利用するものが経済的に有利である。分子状酸素は特に制限されず、純粋な酸素を用いてもよく、窒素、ヘリウム、アルゴン、二酸化炭素などの不活性ガスで希釈した酸素を使用してもよい。操作性及び安全性のみならず経済性などの点から、空気を使用するのが好ましい。

酸素の使用量は、通常、基質1モルに対して、0.5モル以上(例えば、1モル以上)、好ましくは1~100モル、さらに好ましくは2~50モル程度である。基質に対して過剰モルの酸素を使用する場合が多く、特に空気や酸素などの分子状酸素を含有する雰囲気下で反応させるのが有利である。

#### 【0060】

酸化方法は、通常、反応に不活性な有機溶媒中で行なわれる。有機溶媒としては、例えば、酢酸などの有機カルボン酸やオキシカルボン酸、アセトニトリル、ベンゾニトリルなどのニトリル類、ホルムアミド、アセトアミド、ジメチルホルムアミド(DMF)、ジメチルアセトアミドなどのアミド類、*t*-ブータノール、*t*-アミルアルコールなどのアルコール類、ヘキサン、オクタンなどの脂肪族炭化水素、ベンゼンなどの芳香族炭化水素、ハロゲン化炭化水素、ニトロ化合物、酢酸エチルなどのエステル類、ジエチルエーテル、ジイソプロピルエーテル、ジオキサンなどのエーテル類、これらの混合溶媒など挙げられる。

#### 【0061】

反応をプロトン酸の存在下で行なうと、酸化反応を円滑に行なうことができ、高い選択率および收率で目的化合物を得ることができる。このプロトン酸は、前記のように溶媒として用いてもよい。プロトン酸としては、有機酸(ギ酸、酢酸

、プロピオン酸などの有機カルボン酸、シュウ酸、クエン酸、酒石酸などのオキシカルボン酸、メタンスルホン酸、エタンスルホン酸などのアルキルスルホン酸、ベンゼンスルホン酸、p-トルエンスルホン酸などのアリールスルホン酸など）、無機酸（例えば、塩酸、硫酸、硝酸、リン酸など）が含まれる。

## 【0062】

前記酸化触媒又は酸化触媒系を用いる酸化方法は、比較的温和な条件であっても酸化反応が円滑に進行するという特色がある。反応温度は、例えば、0～20℃、好ましくは30～150℃程度であり、通常、50～120℃程度で反応する場合が多い。反応は、常圧または加圧下で行なうことができる。

前記酸化反応において、強酸の存在下で酸化すると、オキソ基を効率よく導入できる。強酸には、前記硫酸やスルホン酸、超強酸などが含まれる。

## 【0063】

カルボキシル基の導入には、種々の反応が利用できるが、酸素に代えて一酸化炭素及び酸素を用いる以外、前記イミド化合物（又はイミド化合物と助触媒）を触媒とする酸化反応と同様の方法（カルボキシル化方法）を用いるのが有利である。カルボキシル化反応で使用される一酸化炭素や酸素は、純粋な一酸化炭素や酸素であってもよく、前記酸化反応と同様に、不活性ガスで希釈して使用してもよい。また、酸素源として空気も使用できる。

## 【0064】

一酸化炭素の使用量は、基質1モルに対して1モル以上（例えば、1～100モル）の範囲から選択でき、好ましくは過剰モルであり、例えば、1.5～100モル（例えば、2～50モル）、さらに好ましくは2～30モル（例えば、5～25モル）程度である。

酸素の使用量は、例えば、基質1モルに対して0.5モル以上（例えば、0.5～100モル）、好ましくは0.5～30モル、さらに好ましくは0.5～25モル程度の範囲から選択できる。

## 【0065】

なお、酸素に対して一酸化炭素を多く用いる方が有利である。COとO<sub>2</sub>との割合は、通常、CO/O<sub>2</sub> = 1/99～99/1（モル%）【例えば、10/9

0~99/1 (モル%) ]、好ましくは30/70~98/2 (モル%)、さらに好ましくは50/50~95/5 (モル%)、特に60/40~90/10 (モル%) 程度である。

ヒドロキシメチル基は、カルボキシル基が導入された基質を、水素や水素化還元剤（例えば、水素化ホウ素ナトリウムールイス酸、水素化アルミニウム、水素化アルミニウムリチウム、水素化トリアルコキシアルミニウムリチウム、ジボランなど）を用いて還元することにより得ることができる。

#### 【0066】

ニトロ基は、慣用の方法、例えば、ニトロ化剤（例えば、硫酸と硝酸との混酸、硝酸、硝酸及び有機酸（例えば、酢酸などのカルボン酸）、硝酸塩及び硫酸、五酸化二窒素など）を用いる方法などにより行うことができる。

好ましいニトロ化方法としては、例えば、前記イミド化合物（又はイミド化合物と助触媒）の存在下又は非存在下、基質と窒素酸化物とを接触させるニトロ化方法が挙げられる。

#### 【0067】

前記窒素酸化物は、式  $N_x O_y$  で表すことができる。

(式中、x は 1 又は 2 の整数、y は 1 ~ 6 の整数を示す)

前記式で表される化合物において、x が 1 である場合、y は通常 1 ~ 3 の整数であり、x が 2 である場合、y は通常 1 ~ 6 の整数である。

#### 【0068】

このような窒素酸化物には、例えば、 $N_2 O$ 、 $NO$ 、 $N_2 O_3$ 、 $NO_2$ 、 $N_2 O_4$ 、 $N_2 O_5$ 、 $NO_3$ 、 $N_2 O_6$  などが例示できる。これらの窒素酸化物は単独で又は二種以上組み合わせて使用できる。

#### 【0069】

好ましい窒素酸化物には、①酸化二窒素 ( $N_2 O$ ) 及び一酸化窒素 ( $NO$ ) から選択された少なくとも一種の窒素化合物と酸素との反応により生成する窒素酸化物（特に  $N_2 O_3$ ）又は  $N_2 O_3$  を主成分として含む窒素酸化物、②二酸化窒素 ( $NO_2$ ) 又は  $NO_2$  を主成分として含む窒素酸化物が含まれる。

窒素酸化物  $N_2 O_3$  は、 $N_2 O$  及び／又は  $NO$  と酸素との反応で容易に得るこ

とができる。より具体的には、反応器内に一酸化窒素と酸素とを導入して、青色の液体  $N_2O_3$  を生成させることにより調製できる。そのため、 $N_2O_3$  を予め生成させることなく、 $N_2O$  及び／又は  $NO$  と酸素とを反応系に導入することによりニトロ化反応を行ってもよい。

なお、酸素は純粋な酸素であってもよく、不活性ガス（二酸化炭素、窒素、ヘリウム、アルゴンなど）で希釈して使用してもよい。また、酸素源は空気であってもよい。

#### 【0070】

他の態様において、窒素酸化物のうち二酸化窒素 ( $NO_2$ ) を用いると、酸素の非共存下でもニトロ化反応が円滑に進行する。そのため、 $NO_2$  を用いる反応系では、酸素は必ずしも必要ではないが、 $NO_2$  は酸素との共存下で使用してもよい。

#### 【0071】

前記イミド化合物（又はイミド化合物と助触媒）を触媒とする酸化方法において、酸素に代えて窒素酸化物（又は窒素酸化物と酸素）を用いる以外、上記酸化方法と同様にしてニトロ化する方法を用いるのが有利である。

#### 【0072】

窒素酸化物の使用量は、ニトロ基の導入量に応じて選択でき、例えば、基質1モルに対して1～50モル、好ましくは1.5～30モル程度の範囲から選択でき、通常、2～25モル程度である。

#### 【0073】

前記イミド化合物で構成された触媒を用いると、ニトロ化反応は、比較的温和な条件であっても円滑に進行する。反応温度は、イミド化合物や基質の種類などに応じて、例えば、0～150°C、好ましくは25～125°C、さらに好ましくは30～100°C程度の範囲から選択できる。ニトロ化反応は、常圧又は加圧下で行うことができる。

#### 【0074】

基質に導入されたニトロ基は還元反応に供することによりアミノ基に変換できる。還元反応は、慣用の方法、例えば、還元剤として水素を用いる接触水素添加

法、水素化還元剤を用いる還元法などにより行うことができる。

接触水素添加法では、触媒として、例えば、白金、パラジウム、ニッケル、コバルト、鉄、銅などの金属単体や、これらの金属元素を含む化合物（例えば、酸化白金、パラジウム黒、パラジウム炭素、亜クロム酸銅など）を用いることができる。触媒の使用量は、アダマンタン類（基質）1モルに対して、通常、0.02～1モル程度である場合が多い。また、接触水素添加法では、反応温度は、例えば、-20～100°C（例えば、0～70°C）程度であってもよい。水素圧は、通常、1～10気圧である場合が多い。

#### 【0075】

水素化還元剤を用いる還元法において、用いられる水素化還元剤としては、例えば、水素化アルミニウム、水素化ホウ素ナトリウム、ジボランなどが挙げられる。水素化還元剤の使用量は、基質1モルに対して、通常、1モル以上（例えば、1～10モル程度）である場合が多い。水素化還元剤を用いる還元法において、反応温度は、通常、0～200°C（例えば、0～170°C）程度である場合が多い。

前記還元反応（接触水素添加法、水素化還元剤を用いる方法）は、還元反応に不活性な溶媒（前記酸化反応の項で例示の溶媒、例えば、カルボン酸、エーテル類、エステル類、アミド類など）の存在下で行ってもよい。

#### 【0076】

なお、基質に導入されたヒドロキシル基は、慣用の方法でアルコキシ基に変換でき、カルボキシル基は慣用のエステル化反応、アミド化反応などをを利用してアルコキシカルボニル基、カルバモイル基、N-置換カルバモイル基に変換できる。さらに、アミノ基はアルキル化剤、アシル化剤などを用いてN-置換アミノ基に変換できる。

#### 【0077】

塩基性基、酸性基を有する化合物や重合体は、塩を形成してもよい。例えば、カルボキシル基含有基質は、有機塩基、無機塩基との反応により塩を形成することができる。アミノ基含有基質は、無機酸、有機酸との反応により塩を形成することができる。

## 【0078】

なお、酸化反応などの反応は、バッチ式、セミバッチ式、連続式のいずれの方式でも行うことができる。反応終了後、反応生成物は、慣用の方法により、容易に分離精製できる。

## 【0079】

## 【発明の効果】

本発明の酸感応性化合物は、脂環族炭化水素基（アダマンタン骨格など）を有し、かつ光照射によりアルカリ可溶性となるので、フォトレジストとして微細なパターンを形成するのに有用である。また、感度および耐エッチング性（特に耐ドライエッティング性）が高く、微細なレジストパターンを安定かつ高い精度で形成できる。さらには、基板に対する密着性を向上させることもでき、高い精度で微細なレジストパターンを安定して形成できる。

## 【0080】

## 【実施例】

以下に、実施例に基づいて本発明をより詳細に説明するが、本発明はこれらの実施例により限定されるものではない。

## 実施例1

## (1) ヒドロキシル化

アダマンタン-1-イル-エタン-1-オン 1モルの無水テトラヒドロフラン溶液に、イソプロピルマグネシウムヨード (iso-C<sub>3</sub>H<sub>7</sub>MgI) 1.2モルの無水ジエチルエーテル溶液を滴下し、10℃で6時間攪拌し、1-(2-ヒドロキシイソペンチル)アダマンタンを得た。

## (2) エステル化

得られた1-(2-ヒドロキシイソペンチル)アダマンタン1.00ミリモル、ヨウ化サマリウム (SmI<sub>2</sub>) 0.10ミリモル、アクリル酸イソプロペニル 1.1ミリモル、ジオキサン (2mL) の混合溶液を50℃で6時間攪拌した。ガスクロマトグラフィーによる分析の結果、反応混合液中には、1-(2-アクリロイルオキシイソペンチル)アダマンタン（収率90%）が生成していた。

マススペクトルデータ [M] 276, 261, 246, 231, 218  
, 191, 147

### (3) 重合

得られた1-(2-アクリロイルオキシイソペンチル)アダマンタン50重量%とメタクリル酸メチル10重量%とアクリル酸ブチル20重量%とメタクリル酸20重量%の単量体混合物100重量部を、重合開始剤(ベンゾイルパーオキサイド)5重量部を用いて有機溶媒(トルエン)中で重合し、混合液にメタノールで添加して重合体を沈殿させた。トルエンに溶解させてメタノールで沈殿させる操作を繰り返して精製し、重量平均分子量約 $1.5 \times 10^4$  (GPCによるポリスチレン換算分子量)の共重合体を得た。

### 【0081】

#### 実施例2

##### (1) ヒドロキシル化

1-(2-アクリロイルオキシイソペンチル)アダマンタン 10ミリモル、N H P I 2ミリモル、コバルトアセチルアセトナトC<sub>o</sub>(AA)<sub>2</sub> 0.1ミリモル、酢酸25mlの混合物を、酸素雰囲気下、75℃で6時間攪拌したところ、1-ヒドロキシ-5-(2-アクリロイルオキシイソペンチル)アダマンタン(収率78%)が得られた。

ヒドロキシル基含有化合物のマススペクトルデータ [M] 292, 274, 259, 244, 229, 216, 189, 145

##### (2) 重合

1-(2-アクリロイルオキシイソペンチル)アダマンタンに代えて、1-ヒドロキシ-5-(2-アクリロイルオキシイソペンチル)アダマンタンを用いる以外、実施例1のステップ(3)と同様にして共重合体を得た。

### 【0082】

#### 実施例3

##### (1) カルボキシル基の導入

アダマンタン-1-イル-エタン-1-オン 10ミリモル、N H P I 1ミリモル、C<sub>o</sub>(AA)<sub>2</sub> 0.005ミリモルを酢酸25ml中に仕込み、混合

ガス (2 L の一酸化炭素と、0.5 L の酸素との混合ガス；圧力: 5 kg/cm<sup>2</sup>) を封入したガスパックを反応器へ接続し、60°Cで6時間攪拌したところ、転化率78%で、1-カルボキシアダマンタン-5-イル-エタン-1-オン (収率62%)を得た。

アダマンタン-1-イル-エタン-1-オンに代えて、1-カルボキシアダマンタン-5-イル-エタン-1-オンを用いる以外、実施例1のステップ(1)と同様にして、1-カルボキシ-5-(2-ヒドロキシ-2-イソペンチル)アダマンタン (収率60%) が得られた。

#### 【0083】

##### (2) (3) エステル化および重合

1-(2-ヒドロキシイソペンチル)アダマンタンに代えて、1-カルボキシ-5-(2-ヒドロキシ-2-イソペンチル)アダマンタンを用いる以外、実施例1のステップ(2) (3)と同様にして、カルボキシル基含有化合物としての1-カルボキシ-5-(2-アクリロイルオキシ-2-イソペンチル)アダマンタン (収率82%) および共重合体を得た。

#### 【0084】

カルボキシル基含有化合物のマススペクトルデータ [M] 320, 24

9, 234, 219, 204, 191, 179, 134

#### 実施例4

##### (1) ヒドロキシル化

アダマンタン-1-イル-エタン-1-オンに代えて、アダマンタノンを用いる以外、実施例1のステップ(1)と同様にして、転化率76%で2-イソプロピル-2-ヒドロキシアダマンタン (収率61%)を得た。

#### 【0085】

##### (2) (3) エステル化および重合

1-(2-ヒドロキシイソペンチル)アダマンタンに代えて、2-イソプロピル-2-ヒドロキシアダマンタンを用いる以外、実施例1のステップ(2) (3)と同様にして、ヒドロキシル基含有化合物としての2-イソプロピル-2-アクリロイルオキシアダマンタン (収率78%) および共重合体を得た。

を得た。

ヒドロキシル基含有化合物のマススペクトルデータ [M] 248, 233, 218, 205, 183, 139。

【0086】

実施例5

(1) ヒドロキシル化

1-(2-アクリロイルオキシイソペンチル)アダマンタンに代えて、2-イソプロピル-2-アクリロイルオキシアダマンタンを用いる以外、実施例2のヒドロキシル化ステップ(2)と同様にして、1-ヒドロキシ-4-イソプロピル-4-アクリロイルオキシアダマンタン(収率56%)を得た。

ヒドロキシル基含有化合物のマススペクトルデータ [M] 264, 246, 231, 216, 203, 176, 132。

(2) 重合

1-(2-アクリロイルオキシイソペンチル)アダマンタンに代えて、1-ヒドロキシ-4-イソプロピル-4-アクリロイルオキシアダマンタンを用いる以外、実施例1のステップ(3)と同様にして共重合体を得た。

【0087】

実施例6

(1) カルボキシル基の導入

アダマンタン-1-イル-エタン-1-オンに代えて、アダマンタノンを用いる以外、実施例3のカルボキシル化ステップ(1)と同様にして、1-カルボキシアダマンタン-4-オンを得た。

アダマンタン-1-イル-エタン-1-オンに代えて、1-カルボキシアダマンタン-4-オンを用いる以外、実施例1のステップ(1)と同様にして、1-カルボキシ-4-(2-ヒドロキシ-2-イソペンチル)アダマンタン(収率58%)が得られた。

【0088】

(2) (3) エステル化および重合

1-(2-ヒドロキシイソペンチル)アダマンタンに代えて、1-カルボキシ

-4-(2-ヒドロキシ-2-イソペンチル)アダマンタンを用いる以外、実施例1のステップ(2)(3)と同様にして、カルボキシリ含有化合物としての1-カルボキシ-4-(2-アクリロイルオキシ-2-イソペンチル)アダマンタン(収率81%)および共合体を得た。

## 【0089】

カルボキシリ含有化合物のマススペクトルデータ [M] 292, 221, 206, 191, 178, 133

## [フォトレジスト用樹脂組成物]

得られた重合体100重量部と、トルフェニルスルホニウムヘキサフルオロアノチモン15重量部と、溶媒トルエンとを混合し、フォトレジスト用樹脂組成物を調製した。このフォトレジスト用樹脂組成物をシリコンウェハーにスピンドティングにより塗布し、厚み1.0  $\mu$ mの感光層を形成した。ホットプレート上で60°Cで100秒間プリベークした後、KrFエキシマステッパを用い、照射量100mJ/cm<sup>2</sup>で露光した後、温度100°Cで60秒間ベークした。次いで、アルカリ水溶液(東京応化(株)製、NMD-3)を用いて60秒間現像し、純水でリノスしたところ、所定のパターンが形成できた。

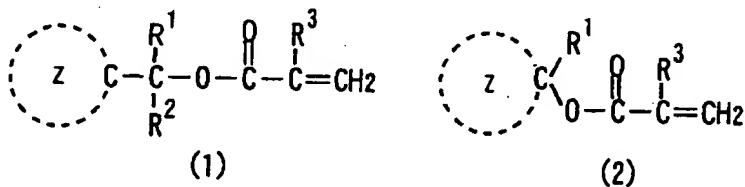
【書類名】 要約書

### 【要約】

【課題】 耐エッチング液性が高く、光照射により可溶化できるフォトレジスト用樹脂組成物により微細なパターンを形成する。

【解決手段】 フォトレジスト用樹脂組成物は、下記式で表される酸感応性化合物の単位（アダマンタン骨格など）を有する重合体と、光酸発生剤とで構成されている。 $R^1$  は、通常、1-位に第3炭素原子を有しており、環乙は、2~4の環を含む架橋環式炭化水素環である。

【化 1】



(式中、 $R^1$  は第3炭素原子を有する分岐鎖状アルキル基、 $R^2$  は水素原子又はアルキル基、 $R^3$  は水素原子又はメチル基、環乙は置換基を有していてもよい単環又は多環式脂環族炭化水素環を示す)

【選択図】 なし

【書類名】 職権訂正データ  
【訂正書類】 特許願

＜認定情報・付加情報＞

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